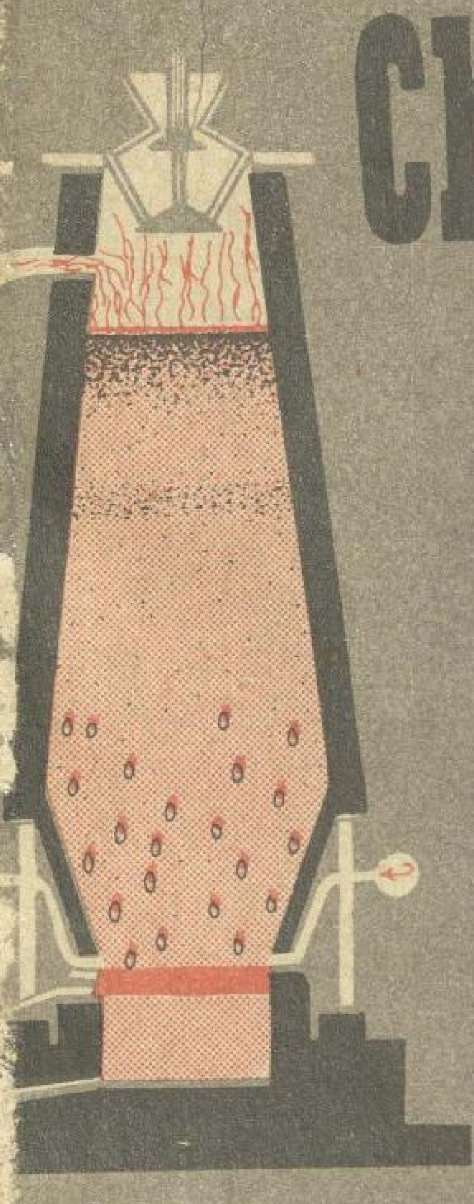

Chemistry

PART II

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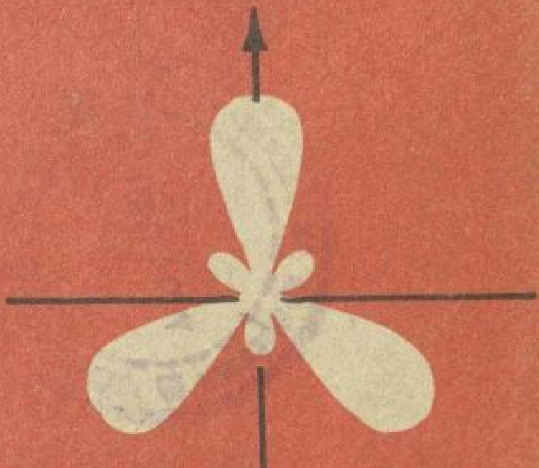

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CHEMISTRY

PART II

FOR CLASS XII

REVIEWED AND REVISED EDITION

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PREFACE

This Text has been written to cover the Chemistry course for class XII adopted in the 2nd phase of modernization of chemistry curricula by the Board of Intermediate and Secondary Education, Peshawar. The revision of the course-content in the subject of Chemistry at the Intermediate level has been made in the light of experience gained in the implementation of the new course during the first phase of modernization (1967 – 72). Many helpful suggestions and criticisms of the College chemistry-teachers have been incorporated in writing the new Text with a view to improving upon the old book.

Five, out of the ten authors, are college teachers with long experience in teaching chemistry to Intermediate classes. A panel of College and University teachers as authors have tried to produce a modern textbook in chemistry to suit the level of the Intermediate course in chemistry.

The basic principles and concepts, such as structure of atom and molecule, chemical bonding, chemical kinetics, chemical equilibrium, chemical thermodynamics and structure of gases, liquids and solids introduced and developed in the text for class XI, have been applied in discussing the chemistry of chemical elements and their compounds in the present book. Emphasis is placed on the understanding of the subject matter rather than stress on memory only. Thus a comparative approach has been adopted in discussing the descriptive chemistry of elements and their compounds.

The text begins with discussion of the periodic classification of elements in Chapter 1 . The basis of modern classification, the correlation of periodic classification and the periodic properties with the atomic structure and the periodicity of some fundamental properties like Atomic size, Ionization energy, electron affinity and electronegativity have been discussed. In terms of these fundamental properties the similarities and variations in the properties of members of each group of elements have been explained.

Chapters 2 to 9 deal with Typical elements, while in chapters 10 and 11 the transition elements and noble gases are discussed respectively.

Chapters 12 to 20 are devoted to the chemistry of Organic compounds keeping in view their enormous number and characteristic properties as group which are not commonly observed in the so-called inorganic compounds. The chapter on the nature of chemical bond included in the old text has been omitted in the present text as it was considered mostly a repetition and duplication of the topic already discussed in the chemistry book for class XI. However, the principles of chemical bonding as applied to the formation and sterio chemistry of Organic compounds such as formation of single, double and triple bonds by carbon atoms and the structure of organic molecules have been discussed at relevant places.

The mechanistic approach has been adopted to explain the chemical reactions of organic compounds. This will be helpful in better understanding of the subject by the students. It will also create a sense of inquisitiveness and inquiry in the readers.

Chemistry of the important industrial processes used for the manufacture of elements and their compounds have been discussed in detail. This will enable the students to acquaint themselves with the useful role of chemistry in the service of man and society.

Numerous questions have been provided at the end of each chapter. These are meant to test the students' understanding of concepts and recall of facts. Some of these questions are objective types.

We are grateful to the learned authors, whose names are given to the beginning of the book, for their valuable co-operation. We wish to acknowledge the assistance of Dr. M. A. Khawaja for reading a substantial part of the typed manuscript. We would also like to thank the authorities of the Board of Intermediate and Secondary Education , Peshawar and the N. W. F. P. Textbook Board for their help and assistance in the preparation and the publication of this textbook.

The authors and editors will gratefully welcome suggestions and criticisms from the students and teachers for further improvement in the textbook and the syllabus.

S. MARGHOOB ALI
N. A. ZAIDI

CHAPTER 1

PERIODIC CLASSIFICATION OF ELEMENTS

Basis of Classification:

So far 105 elements have been discovered. More may be discovered in future. It is impossible to study each element separately. To make our work easier, similar elements may be grouped together. If we study one typical element of the group, we shall know most of the properties of the other members of the group.

When we try to classify things, we have to select some property as the basis of this classification. In the olden times elements were classified as Metals and Non-metals. But there is no clear cut line dividing metals from Non-metals. Some elements behave both as Metals and as Non-Metals.

In 1869, the Russian chemist Mendeleef devised the first useful classification system for elements called the Periodic Table of Elements. In this table the elements were arranged in the order of increasing atomic weights. He thus noticed that the chemical properties of the elements recurred at definite intervals. From this he concluded "the properties of the elements were the periodic function of their atomic weights". This is known as Mendeleef's Periodic Law.

Later on, the study of the Positive Rays showed that all the atoms of the same element may not have equal weights. In fact, atoms of the same element may have many different weights. These are called *"Isotopes"*. The discovery of isotopes proved that "Atomic Weight" is not, after all, a fundamental property of the elements.

Study of the structure of atom showed that the number of positive charges on the nucleus of the atom of an element is a very important property of the element. It is called *"Atomic Number"*. Each element can be recognised by its Atomic Number. All the Isotopes of an element have the same Atomic Number.

About 1914 a British Scientist, G.F. Moseley, showed that the wavelength of X-rays emitted by each element depend upon its atomic number. The higher the atomic number of the element, the shorter is the wavelength of the X-rays emitted. Atomic Number is, therefore, a fundamental property of the elements.

The Modern Periodic Law:

If elements are arranged in the order of their increasing Atomic Numbers, elements possessing similar properties occur at regular intervals. Repetition of a property at regular intervals is called periodicity of that property. Night and day, season of the years, movement of the pendulum of a clock are all periodic events. They repeat themselves at regular intervals.

The modern classification of elements is based on atomic numbers and the periodic law may be restated as "The physical and chemical properties of the elements are periodic function of their Atomic Numbers".

The Modern Periodic Tables:

Based on atomic numbers many forms of the Periodic Table have been prepared. The one form of the Periodic Table which is in common use is shown in Fig. 1.1.

An element is presented by its symbol in the Table. Atomic Numbers and Atomic Weights are shown above and below the symbol respectively. Horizontal row of elements in the Table is called a *Period*, while a vertical

PERIODIC TABLE OF THE ELEMENTS

Group Period	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII B			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	Light metals								H 1.008						Non metals			2 He 4.003
2	3 Li 6.940	4 Be 9.013	Heavy metals										5 B 10.82	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Nc 20.18
3	11 Na 23.00	12 Mg 24.32											13 Al 26.97	14 Si 28.06	15 P 30.98	16 S 32.07	17 Cl 35.46	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 45.10	22 Ti 47.9	23 V 50.90	24 Cr 52.01	25 Mn 54.93	26 Fe 55.85	27 Co 58.94	28 Ni 58.69	29 Cu 63.54	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Sc 78.96	35 Br 79.92	36 Kr 83.7
5	37 Rb 85.48	38 Sr 87.63	39 Y 88.9	40 Zr 91.29	41 Nb 92.91	42 Mo 95.95	43 Tc 99	44 Ru 101.7	45 Rh 102.9	46 Pd 106.7	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.7	52 Te 127.6	53 I 126.9	54 Xc 131.3
6	55 Cs 132.9	56 Ba 137.4	57* La 138.9	72 Hf 178.6	73 Ta 180.9	74 W 183.9	75 Re 186.3	76 Os 190.2	77 Ir 193.1	78 Pt 195.2	79 Au 197.2	80 Hg 200.8	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 210	85 At 211	86 Rn 222
7	87 Fr 223	88 Ra 226.1	89** Ac 227	104 Ku 257	105 Ha 260													

Lanthanide Series*	58 Ce 140.1	59 Pr 140.9	60 Nd 144.3	61 Pm 146	62 Sm 150.4	63 Eu 152.0	64 Gd 156.9	65 Tb 159.2	66 Dy 162.5	67 Ho 164.9	68 Er 167.2	69 Tm 169.4	70 Yb 173.0	71 Lu 175.9
Actinide Series**	90 Th 232.1	91 Pa 231	92 U 238.1	93 Np 237	94 Pu 239	95 Am 241	96 Cm 242	97 Bk 243	98 Cf 244	99 Es 254	100 Fm 257	101 Md 258	102 No 253	103 Lw 257

Table. 1.1

PERIODIC TABLE OF ATOMIC RADII

0.32 H I																	0.31 He 2
I	II											III	IV	V	VI	VIII	
1.23 Li 3	0.89 Be 4											0.82 B 5	0.77 C 6	0.75 N 7	0.73 O 8	1.72 F 9	0.71 Ne 10
1.54 Na 11	1.36 Mg 12											1.18 A1 13	1.11 Si 14	1.06 P 15	1.02 S 16	0.99 Cl 17	0.98 Ar 18
2.03 K 19	1.74 Ca 20	1.44 Sc 21	1.32 Ti 22	1.22 V 23	1.18 Cr 24	1.17 Mn 25	1.17 Fe 26	1.16 Co 27	1.15 Ni 28	1.17 Cu 29	1.25 Zn 30	1.26 Ga 31	1.22 Ge 32	1.20 As 33	1.17 Se 34	1.14 Br 35	1.12 Kr 36
2.16 Rb 37	1.91 Sr 38	1.62 Y 39	1.45 Zr 40	1.34 Nb 41	1.30 Mo 42	1.27 Tc 43	1.25 Ru 44	1.25 Rh 45	1.28 Pd 46	1.34 Ag 47	1.48 Cd 48	1.44 In 49	1.40 Sn 50	1.40 Sb 51	1.36 Te 52	1.33 I 53	1.31 Xe 54
2.35 Cs 55	1.98 Ba 56	1.56 Lu 71	1.44 H1 72	1.34 Ta 73	1.30 W 74	1.28 Re 75	1.26 Os 76	1.27 Ir 77	1.30 Pt 78	1.34 Au 79	1.49 Hg 80	1.48 T1 81	1.47 Pb 82	1.46 Bi 83	1.46 Po 84	1.45 At 85	Rn 86
Fr 87	2.20 Ra 88	Lw 103	Ku 104														

1.69 La 57	1.65 Ce 58	1.64 Pr 59	1.64 Nd 60	1.63 Pm 61	1.62 Sm 62	1.85 Eu 63	16.2 Gd 64	1.61 Tb 65	1.60 Dy 66	1.58 Ho 67	1.58 Er 68	1.58 Tm 69	1.70 Yb 70
Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102

Table 1.2

column of elements constitutes a Group or a Family. There are seven periods in the table and eighteen groups or families.

The first period contains two elements, Hydrogen and Helium. Hydrogen, atomic number 1, is placed at the top of the Table by itself because of its many unique properties. It has one electron in the 1st shell. Helium, atomic number 2, is at the top of the extreme right hand column. There are two electrons in the "k" shell of Helium, and with that the "K" shell is completely filled.

The second period consists of eight elements from Lithium atomic number 3 to Neon, atomic number 10. The third period also contains 8 elements. The elements of 1st, 2nd and 3rd periods are called *Typical Elements.* In these elements, distinguishing electrons enter the "s" or "p" sub-shell. The fourth and fifth periods have 18 elements, while the number of elements in the sixth period is 32. The seventh period is at present incomplete.

The fourth and subsequent periods are known as long periods. In the fourth and fifth periods, in addition to eight typical elements, there are ten *Transition elements.* In the later elements the distinguishing electrons enter the "d" sub-shell. In the sixth period there are eight typical elements, ten transition elements and fourteen *rare-earth* elements. These rare earths are also called the Lanthanides. In these elements distinguishing electrons enter the "f" sub-shell.

The seventh period is supposed to be similar to the sixth period. The fourteen rare earth elements in this period are known as the Actinides. So far only 19 elements have been discovered in this period.

Each vertical column of the table constitutes a group and contains elements with similar properties. Group IA of the periodic table is called the Alkali Metal family. They are group of six similar, very active, metallic elements. They all have one electron in their outer-most shell. The similarity in their physical and chemical properties is due to their similar electronic configuration.

Group IIA also consists of six active metals whose chemical properties are very much alike. Each one of these has 2 electrons in the outer-most shell. Similarly the members of the group IIIA, IVA, VA, VIA and VIIA have three, four, five, six and seven electrons respectively in their outer-most shells. Each group consists of similar elements with gradual variation from non-metallic to metallic properties as we go down the group. For example in group VA Nitrogen and Phosphorus, which occur at the top of the table, are non-metallic. Arsenic and Antimony exhibit both metallic and non-metallic properties. While Bismuth at the bottom of the table, is metallic. Elements like Arsenic and Antimony, which show both metallic and non-metallic properties under different conditions are known as Metalloids.

Group VIIIA is the Noble Gas family. With the exception of helium atom which has a pair of electrons in its outer-most shell, atoms of these elements have an octet in their outermost shell. Because of their complete outer shell, these elements are mostly chemically inert. However, a few compounds of Krypton, Xenon and Radon have been prepared.

The members of the Groups IIIB, IVB, VB, VIB, VIIB, VIIIB (Three vertical columns), IB and IIB constitute the Transition elements. These are metallic elements showing variable valency. They form coloured compounds and act as catalysts. Members of the Group VIIIB show close similarity in properties both in vertical and horizontal directions.

Electronic Configuration and the Periodic Table:

There is a close relationship between the electronic configuration of an element and its properties. A detailed description of electronic configuration of elements has been given in part I of this book (Chapter 3). At this point it would, however, be useful to describe briefly the relationship between the electronic configuration and properties of elements:

In the first period there are two elements Hydrogen and Helium with atomic number 1 and 2 respectively. The electronic structure of Hydrogen is IS^1, while that of Helium is IS^2. Thus K shell is completely filled.

The first element of the second period is Lithium ($Z = 3$) with electronic configuration $IS^2, 2S^1$. In subsequent elements, Be, B, C, N, O, F, and Ne, the electrons are progressively added until 2P sub-shell has six electrons and shell gets completed.

$^4Be - IS^2, 2S^2$; $^5B - IS^2, 2S^2, 2P^1$; $^6C - IS^2, 2S^2, 2P^2$

$^7N - IS^2, 2S^2, 2P^3$; $^8O - IS^2, 2S^2, 2P^4$; $^9F - IS^2, 2S^2, 2P^5$;

$^{10}Ne - IS^2, 2S^2, 2P^6$.

As the electronic configuration varies progressively, so do the properties of elements in the period. Thus we see that the metallic and electropositive character gradually changes from Lithium to Fluorine. Lithium is an active electropositive element on the extreme left in the period, while Fluorine is the most electronegative non-metal at the right end of the period.

The third period also contains eight elements and their electronic configuration can be built up on the same pattern as those of the elements in the 2nd period.

Within a group or family, elements have similar electronic configuration and therefore show similar properties. The members with higher atomic numbers have outer electrons in the higher Quantum shells. As an example the electronic configuration of alkali metal family (Group IA) is detailed below:

$^3Li = IS^2, 2S^1$

$^{11}Na = IS^2, 2S^2, 2P^6, 3S^1$

$^{19}K = IS^2, 2S^2, 2P^6, 3S^2, 3P^6, 4S^1$

$^{37}Rb = IS^2, 2S^2, 2P^6, 3S^2, 3P^6, 3d^{10}, 4S^2, 4P^6, 5S^1$

$^{55}Cs = IS^2, 2S^2, 2P^6, 3S^2, 3P^6, 3d^{10}, 4S^2, 4P^6, 4d^{10}, 5S^2, 5P^6, 6S^1$

$^{87}Fr = IS^2, 2S^2, 2P^6, 3S^2, 3P^6, 3d^{10}, 4S^2, 4P^6, 4d^{10}, 4f^{14}, 5S^2, 5P^6$
$5d^{10}, 6S^2, 6P^6, 7S^1$.

All these elements have nS^1 electron in the outer-most or valency shell and therefore show similar chemical properties. Going down the group the value of n progressively increases resulting in the increase of the size of the atom. Thus the reactivity and electropositive character increases from Lithium to Francium.

Periodicity of Properties:

According to the Periodic Law, properties of elements should show periodic behaviour with increasing atomic number. There are certain basic properties such as Atomic size, Ionization Energy, Electonegativity and Electron Affinity which determine the other properties of elements. We will in this chapter discuss the periodic variation of these properties.

ATOMIC SIZES

The apparent size of an atom or its radius can be determined from X-ray and Spectral studies of bound atoms. It is equal to one half of the distance between adjacent nuclei of atoms. The atomic radii are shown in Table. 1.2. They are measured in Angstrom units ($1^{\circ}A = 10^{-8}$ cm).

In general the atomic radii decrease in going from left to right across the periodic table and increase in going from top to bottom. The decrease in atomic radius across a period is due to greater attraction of the increasing nuclear charge for the electron entering the same shell, thus pulling them closer to the nucleus. The increase in atomic radius in a group is because each successive element has one more shell or energy level than the preceding one. Even though the nuclear charge increases and tends to decrease the radii of electron shells by drawing them closer, the addition of a shell more than counter-acts this effect.

Ionization Energy:

The amount of energy required to remove an electron from a gaseous atom is called the Ionization Energy or Ionization Potential. Table 1.3 shows the first Ionization potentials of the elements in the periodic table.

In general the ionization energy increases from left to right within a period and decreases within a group from top to bottom. The increase in the value of ionization energy in a period may be expalined in terms of increase in nuclear charge and decrease in atomic radii from left to right. The decrease in ionization energy with increasing atomic number in a group is due to increased atomic radius.

First Ionization Potentials of the Elements
(in Electron Volts)

1 H 13																	2 He 24.6
3 Li 5.4	4 Be 9.3											5 B 8.3	6 C 11.3	7 N 14.5	8 O 13.6	9 F 17.4	10 Ne 21.6
11 Na 5.1	12 Mg 7.6											13 Al 6.0	14 Si 8.1	15 P 11.10	16 S 10.4	17 Cl 13.0	18 Ar 15.8
19 K 4.3	20 Ca 6.1	21 Sc 6.6	22 Ti 6.8	23 V 6.7	24 Cr 6.8	25 Mn 7.4	26 Fe 7.9	27 Co 7.9	28 Ni 7.6	29 Cu 7.7	30 Zn 9.4	31 Ga 6.0	32 Ge 8.1	33 As 10.0	34 Se 9.8	35 Br 11.8	36 Kr 14.0
37 Rb 4.2	38 Sr 5.7	39 Y *6.6	40 Zr 7.0	41 Nb 6.8	42 Mo 7.2	43 Tc –	44 Ru 7.5	45 Rh 7.7	46 Pd 8.3	47 Ag 7.6	48 Cd 9.0	49 In 5.8	50 Sn 7.3	51 Sb 8.6	52 Te 9.0	53 I 10.4	54 Xe 12.1
55 Cs 3.9	56 Ba 5.2		72 Hf 5.5	73 Ta 6	74 W 8.0	75 Re 7.9	76 Os 8.7	77 Ir 9.2	78 Pt 9.0	79 Au 9.2	80 Hg 10.4	81 Tl 6.1	82 Pb 7.4	83 Bi 8.0	84 Po –	85 At –	86 Rn 10.7
87 Fr –	88 Ra 6.3	+	104 Ku	105 Ha													
		*57 La 5.6	58 Ce 6.9	59 Pr 5.8	60 Nd 6.3	61 Pm –	62 Sm 5.6	63 Eu 5.7	64 Gd 6.2	65 Tb 6.7	66 Dy 6.8	67 Ho –	68 Er –	69 Tm –	70 Yb 6.2	71 Lu 5.0	
		+89 Ac –	90 Th –	91 Pa –	92 U 4	93 Np –	94 Pu –	95 Am –	96 Cm –	97 Bk –	98 Cf –	99 Es –	100 Fm –	101 Md –	102 No –	103 Lw –	

TABLE 1.3

Electron Affinity:

This is the energy released when an electron is added to an isolated neutral atom.

$$X + \bar{e} \longrightarrow \bar{X} + \text{Energy}$$

The electron Affinity indicates how tightly an additional electron is bound to an atom. The values for the halogen elements are given in Table 1.4.

The electron affinities decrease from chlorine to iodine as expected. This is because the additional electron enters the shells, which are increasingly farther from the nucleus. The unexpectedly low value for Fluorine may be due to its very small size.

TABLE 1.4

Electron Affinities of the Halogens

Element	Electron Affinity (K. Cal / mole)
Fluorine	81.0
Chlorine	84.8
Bromine	79.1
Iodine	72.1

Electronegativity:

This is the measure of the power of an atom to attract a shared pair of electrons in a covalent bond. This property like the Ionization Potential and Electron Affinity, depends upon the attraction of the nucleus for the valence electrons. The shorter is the distance between the nucleus and the valency electrons the smaller will be size of the atom and the greater will be the value of Electronegativity. Electronegativity increases across the period and down the group it decreases. In group VII A Fluorine has the highest electronegativity while Iodine has the lowest.

	F	Cl	Br	I
Electronegativity:	4.0	3.0	2.8	2.4

The variation of electronegativity across the 2nd and 3rd periods is shown below:–

Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0

Importance of Periodic table:

In early years the Periodic Table served as a valuable tool to check on atomic weight determinations and for the prediction of new elements. At present, however, this table serves as a useful aid to systematic classification of elements according to their properties and make the study of chemistry easier.

QUESTIONS

1. (a) On what basis did Mendeleef arrange the elements in his Periodic Table?
   (b) On what basis are they arranged today?
   (c) What is the periodic law?

2. (a) Name the elements in the second period.
   (b) How does the number of electrons in the outer shell vary in these elements.
   (c) How do their properties compare?

3. What is similar about the electronic configuration of elements with similar properties?

4. Explain why?
   (a) The radius of an atom is not a definitely fixed quantity.
   (b) Metals have low ionization energy.
   (c) Removal of second electron from an atom requires more energy than the removal of the first.

5. How do the atomic radii of the Group I elements compare with the radii of other elements of their periods?

6. (a) How did Mendeleef know where to leave gaps for undiscovered elements in his Periodic Table?
   (b) How did Moseley know where to leave gaps for undiscovered elements?

7. Why is hydrogen placed separately in the Periodic Table?

8. (a) What are transition elements?
   (b) In which periods of elements do they appear?

9. (a) How does atomic size vary with atomic number within a family of elements?
   (b) Why does it vary this way?

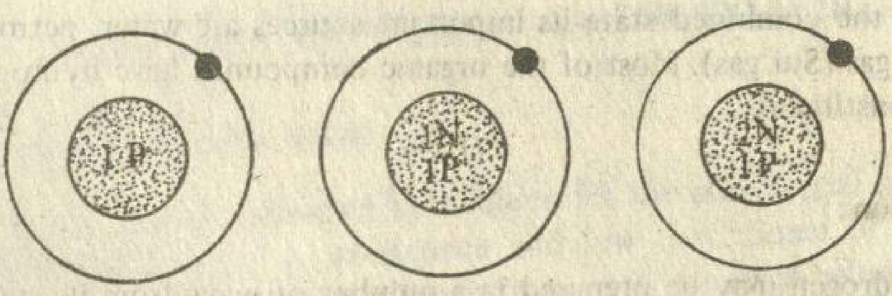
10. (a) Where in a group will you most probably find atoms having the largest ionization potential.
    (b) The largest atomic radius. Explain?

CHAPTER 2

HYDROGEN

Hydrogen is the first element in the periodic table. It has the simplest atomic structure of all the elements.

An atom of hydrogen consists of one proton in the nucleus and an electron in 1S orbital. It is represented by the symbol $^{1}_{1}H$. There are two other isotopes of Hydrogen namely Deutrium $^{2}_{1}D$ or $^{2}_{1}H$ and Tritium, $^{3}_{1}T$ or $^{3}_{1}H$. Deutrium with mass number 2 has one neutron and one proton in the nucleus, while the nucleus of Tritium contains two neutrons and one proton. However, all the three isotopes of hydrogen have the same atomic number (Z=1) and consequently only one electron in the 1S orbital.



Protium **Deuterium** **Tritium**

Three Isotopes of Hydrogen

Fig. 2, 1

Ordinary hydrogen found in nature or prepared in the laboratory contains 99.184% of ${}_{1}^{1}H$ isotopes the rest being the amount of heavier isotopes. Thus the atomic weight of hydrogen (= 1.008) is the average weight of all the three isotopes.

The electronic configuration of hydrogen is similar to that of alkali metals (group IA) in having one S electron in outer orbit. On this basis hydrogen may be classified as a member of group IA. However, hydrogen unlike alkali metals shows a little tendency to lose its valency electron. On the other hand an atom of hydrogen has a greater tendency to pair the electron by sharing it with other atoms and form a covalent bond. In this respect hydrogen resembles the halogen as both have one electron less than an inert gas configuration. Thus hydrogen may also be placed with halogens in Group VIIA.

In view of the unique properties of hydrogen it would be better to place it in a group of its own.

Occurrence:

In the free state hydrogen is found in abundance in Sun and most of the stars. Free hydrogen also occurs in small amount in volcanic gases and earth's atmosphere.

In the combined state its important sources are water, petroleum and natural gas (Sui gas). Most of the organic compounds have hydrogen as one of the constituents.

Preparation:

Hydrogen may be prepared in a number of ways from its compounds. Particularly from acids, bases and water.

1. **Preparation from acids:**

Active metals, which are easily oxidizable by the removal of electrons, *i.e.,* have low electron affinities, low ionization potential and low electronegativity, liberate hydrogen from dilute acids. Typical examples of this type of reactions are:

$$Zn + 2H^{+} + 2Cl^{-} \longrightarrow Zn^{+2} + 2Cl^{-} + H_2 \uparrow$$
$$Zn + 2H^{+} + SO_4^{-2} \longrightarrow Zn^{+2} + SO_4^{-2} + H_2 \uparrow$$
$$Fe + 2H^{+} + 2Cl^{-} \longrightarrow Fe^{+2} + 2Cl^{-} + H_2 \uparrow$$
$$Fe + 2H^{+} + SO_4^{-2} \longrightarrow Fe^{+2} + SO_4^{-2} + H_2 \uparrow$$

Any metals which is more electropositive than hydrogen can displace hydrogen from acid solutions.

In the laboratory hydrogen is usually prepared by this method.

2. Preparation from bases:

Certain elements, such as aluminium, zinc and silicon, react with aqueous solutions of strong bases like sodium hydroxide to liberate hydrogen with the formation of salts:-

$$2Al + 2\overset{+}{Na} + 2\overset{-}{OH} + 6H_2O \longrightarrow \underset{\text{Sodium aluminate}}{2Na[Al(OH)_4]} + 3H_2$$

$$Zn + 2\overset{+}{Na} + 2\overset{-}{OH} + 2H_2O \longrightarrow \underset{\text{Sodium Zincate}}{Na_2[Zn(OH)_4]} + H_2$$

$$Si + 2\overset{+}{Na} + 2\overset{-}{OH} + H_2O \longrightarrow Na_2SiO_3 + 2H_2$$

3. Preparation from water:

Water is generally used as a source for the commercial preparation of hydrogen because of its abundance and low cost. Some of the methods used for the preparation of hydrogen from water are given below:

(i) **By the electrolysis of water:** Pure water is a poor conductor of electricity. However, water containing a small amount of a strong acid or a strong base such as H_2SO_4 or NaOH becomes a good conductor of electricity and the water splits into its components on the passage of electric current. This process is known as electrolysis of water. The mechanism of the reaction is outlined below:–

$$\begin{tikzcd}
2H_2SO_4 \rightleftharpoons & 4H^+ \arrow[d] & + & 2SO_4^{-2} \arrow[d, "+2H_2O"] \\
& 2H_2 & & 2H_2SO_4 + O_2\uparrow \\
& \text{(Cathode)} & & \text{(Anode)}
\end{tikzcd}$$

$$\begin{tikzcd}
4NaOH \rightleftharpoons & 4Na^+ \arrow[d, "+4H_2O"] & + & 4OH^- \arrow[d] \\
& 4NaOH + 2H_2\uparrow & & 2H_2O + O_2\uparrow \\
& \text{(Cathode)} & & \text{(Anode)}
\end{tikzcd}$$

Hydrogen is liberated at the cathode, while oxygen is obtained at the anode. The over-all reaction is the decomposition of water and may be represented as:–

$$2H_2O + \text{Electrical Energy} \longrightarrow 2H_2\uparrow + O_2\uparrow$$

This process is of commercial importance only in those countries where the cost of elctricity is cheap. It is not yet economically feasible in Pakistan.

(ii) **By the electrolysis of sodium chloride solution**: When an aqueous solution of sodium chloride (common salt) is electrolysed, hydrogen is formed along with sodium hydroxide and chlorine.

$$2Na^+ + 2Cl^- + 2H_2O + \text{Electrical Energy} \longrightarrow \underbrace{2Na^+ + 2OH^-}_{\text{Caustic Soda}} + Cl_2\uparrow + H_2\uparrow$$

This method is used for the commercial production of caustic soda and chlorine, while hydrogen is a by–product (Chapter 9).

(iii) **By the action of metal on water**: Very active metals like sodium, potassium and calcium rapidly displace hydrogen from water at room temperature.

$$2Na + 2HOH \longrightarrow 2\overset{+}{Na} + 2O\overset{-}{H} + H_2\uparrow$$

$$Ca + 2HOH \longrightarrow \underbrace{Ca^{+2} + 2OH^-}_{\text{Calcium hydroxide}} + H_2\uparrow$$

Less active metals like iron and magnesium liberate hydrogen on reaction with steam.

$$Mg + H_2O \longrightarrow MgO + H_2 \uparrow$$

$$3Fe + 4H_2O \longrightarrow 3Fe_3O_4 + 4H_2 \uparrow$$

Reaction of iron with steam is used for the industrial preparation of Hydrogen. The magnetic oxide of iron (Fe_3O_4) on treatment with carbon monoxide regenerates free iron which may be used again:

$$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2 \uparrow$$

(iv) **By passing steam on hot coke**: Carbon (coke) reacts with steam at a high temperature to form a mixture of hydrogen and carbon monoxide (water gas).

$$C + H_2O \longrightarrow \underset{\text{Water gas.}}{CO + H_2}$$

CO is separated from the water gas by the catalytic oxidation to carbon dioxide in presence of ferrous oxide (FeO) and the latter gas is removed by absorption in KOH solution.

$$CO + H_2O \xrightarrow{FeO} CO_2 + H_2$$

$$CO_2 + 2KOH \longrightarrow K_2CO_3 + H_2O$$

This method may also be used on commercial scale.

4. Preparation from natural gas (Sui gas):

Large quantities of hydrogen in Pakistan are obtained for the synthesis of ammonia from Sui gas (a mixture of hydrocarbons containing about 90% methane).

A mixture of steam and purified Natural gas in presence of Nickel as a catalyst produces hydrogen and carbon monoxide.

$$CH_4 + H_2O \xrightarrow{Ni} 3H_2 + CO$$

CO is removed by converting it into CO_2 as described earlier.

Properties:–

Hydrogen is a colourless, odourless and tasteless gas consisting of diatomic molecules. Its physical properties are summarized in Table 2.1

TABLE 2.1

Atomic mass	1.008 a.m.u.
Molecular mass	2.016 a.m.u.
Bond length	0.749 A
Bond energy	104 KCal/Mole
Melting point	14.1°K
Boiling point	20.4°K
Critical temperature	32.2°K
Density at STP	0.089 g/lit

Chemical Properties:

Hydrogen molecule has a covalent bond and therefore in chemical reactions of hydrogen usually the first step is the breaking up of the H–H bond (dissociation energy 104 K Cal/mole). Because of the high dissociation energy of H–H bond the reactions of hydrogen are generally slow.

Hydrogen may react chemically in three different ways:

(i) The hydrogen atom may share its one electron with another atom to form a covalent bond.

$$H_2 + X_2 \longrightarrow 2H : X$$

(X = the atom of another element)

(ii) The hydrogen atom may lose one electron to form a positive ion, H^+

$$\dot{H} \longrightarrow \overset{+}{H} + \bar{e}$$

(iii) The Hydrogen atom may gain an electron to form a negative, $\bar{H}$.

$$\dot{H} + \bar{e} \longrightarrow [\,\bar{H}\,]$$

Of the three possible kinds of reactions, the first one is most common. The second reaction is not energetically favoured because of high ionization potential (13.60 ev), while the last reaction has the limitation of low electron affinity of Hydrogen atom (0.72 ev).

Reactions with non-metals:

Under appropriate conditions, hydrogen combines directly with most non-metals.

$$2H_2(g) + O_2(g) \xrightarrow[\text{or Catalyst}]{\text{High temp.}} 2H_2O(1)\ \Delta H = -136.64\text{K Cal.}$$

Mixtures of hydrogen and oxygen are explosive and need careful handling. In the oxyhydrogen torch the above reaction produces the temperature of about 2,000°C.

With halogens, hydrogen reacts to form halides.

$$H_2(g) + F_2(g) \longrightarrow 2HF(g)\ \Delta H = -130\text{K Cal.}$$

Other examples of the reaction between hydrogen and non-metals are:

$$H_2 + S \longrightarrow H_2S \quad \Delta H = -5.26\text{K Cal.}$$

$$3H_2 + N_2 \longrightarrow 2NH_3 \quad \Delta H = -21.88\text{K Cal.}$$

Reactions with metals:

Hydrogen reacts with almost all metals to form hydrides. The hydrides of some of the active metals are ionic compounds. They are formed at elevated temperature.

$$2Li + H_2 \longrightarrow 2Li^+H^-$$

$$Ca + H_2 \longrightarrow Ca^{+2}2H^-$$

Reduction Reactions:

Hydrogen reduces the oxides of many metals at high temperatures.

$$Fe_2O_3 + 3H_2 \xrightarrow{Heat} 2Fe + 3H_2O$$

$$CuO + H_2 \xrightarrow{Heat} Cu + H_2O$$

Certain metal oxides on reduction form a lower oxide. For example:

$$\overset{IV}{Mn}O_2 + H_2 \xrightarrow{Heat} \overset{II}{Mn}O + H_2O$$

Manganese dioxide Manganous oxide

Hydrogenation Reactions:

Hydrogen simply adds on to certain compounds. Such reactions are called Hydrogenation reactions.

$$CO + 2H_2 \xrightarrow{Catalyst} CH_3OH$$

Vegetable ghee is also prepared by the hydrogenation of unsaturated oils such as cotton seed oil, and soyabeen oil.

Uses:

Some major uses of hydrogen are in oxy-hydrogen flame, hydrogenation of oils, synthesis of ammonia, synthesis of methyl alcohol and the hydrogenation of coal to produce liquid hydrocarbons (Petrol).

Nascent Hydrogen:

The hydrogen at the time of its generation is called Nascent hydrogen. It is more reactive than the ordinary hydrogen. For example, on passing hydrogen gas through an acidified solution of potassium permanganate the latter is not decolourised. However, the acidified potassium permanganate solution gets decolourised, when Zn is added to it due to the formation of Nascent hydrogen.

(i) $[Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2H] \times 5$

(ii) $2KMnO_4 + 3H_2SO_4 + 2H \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O$

QUESTIONS

1. What is the Atomic Structure of Hydrogen?
   In what way is the Hydrogen nucleus unique?

2. Name three metals that will displace hydrogen from:

   (a) cold water (b) steam (c) acid. Give equations.

3. What is the Nascent Hydrogen? Give its reactions.

4. Write the name and structure of each of the three isotopes of Hydrogen.

CHAPTER 3

WATER

Introduction:

Water is the most extensively found compound in nature. It is found in Oceans, Rivers, Lakes etc. It is also found in large quantities below the soil and in the form of water vapours in the atmosphere. It exists in three states namely solid (ice), liquid (water) and gaseous (water vapours). It forms 65% by weight of human body and to a variable extent it is also present in the plant kingdom. It is a very important compound because of its abundance and unique properties.

Physical Properties:

It is a colourless and tasteless compound. Its physical contants are given below:--

Freezing point	0°C
Boiling point under one atmosphere pressure	100°C
Density at 3.98°C	1.00 gm/ml
Heat of fusion	79.7 Cal/g
Heat of vaporization	539.6 Cal/g
Specific heat.	1.00 Cal/g/C°

Water, unlike other liquids which contract on cooling, shows anomalous behaviour. When water is cooled from 100°C its density gradually increases from 0.9584 g/ml to 1.000 at 3.98°C (or 4°C) upto this point water behaves as other liquids. However on further cooling the effect reverses and the density now gradually decreases, reaching the value of 0·9998 g/ml at 0°C. At this temperature liquid water freezes into ice and the density decreases to 0.917 g/ml (density of ice.) Thus ice is lighter than water and, therefore, floats on it. The liquid water, therefore, has maximum density at 3.98°C.

Figure 3.1 show the change of the density of water with the change of temperature.

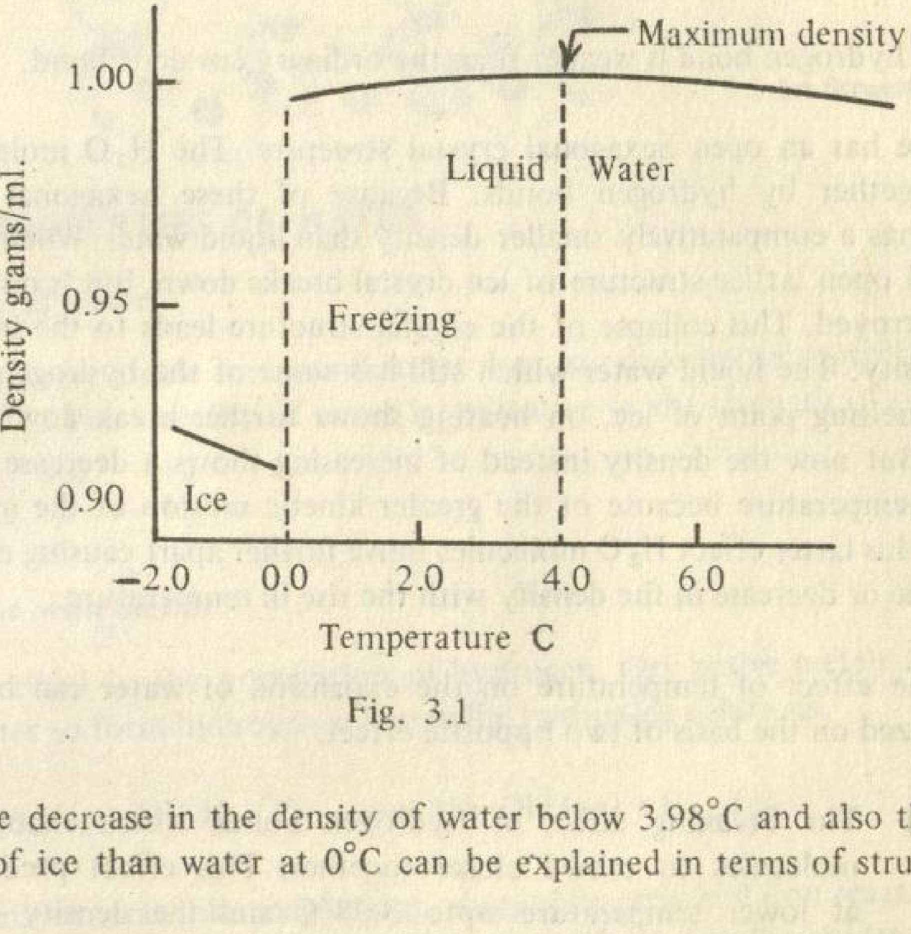
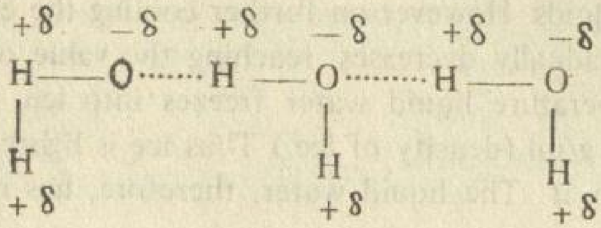


Fig. 3.1

The decrease in the density of water below 3.98°C and also the lesser density of ice than water at 0°C can be explained in terms of structure of water.

The water molecules are non-linear with polar covalent bonds and bond angle of 104.5°.

Because of polarity of water molecules, H atom (with a + ve charge) of one molecule and the O atom (with a −ve charge) of the other molecule get associated with each other forming three dimensional groups of molecules:



Such a bond in which two hydrogen atoms serve as a link between two electronegative atoms, like oxygen, is called a hydrogen bond.

A hydrogen bond is weaker than the ordinary covalent bond.

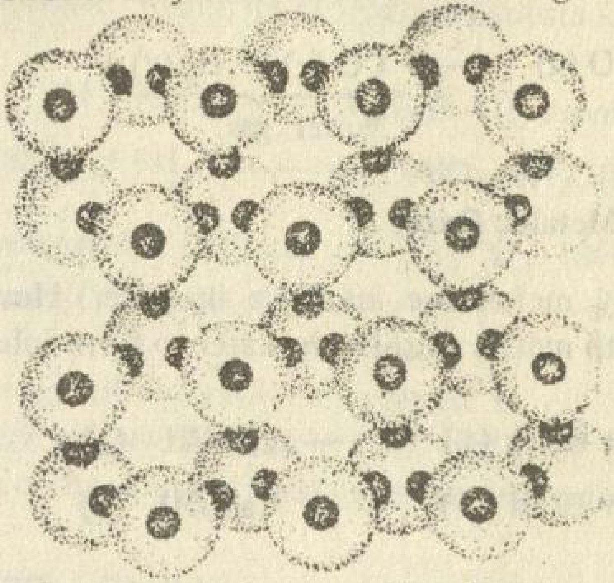
Ice has an open hexagonal crystal structure. The H_2O molecules are held together by hydrogen bonds. Because of these hexagonal channels the ice has a comparatively smaller density than liquid water. When ice melts the rigid open lattice-structure of ice crystal breaks down, but is not completely destroyed. This collapse of the crystal structure leads to the increase in the density. The liquid water which still has some of the hydrogen bonding at the melting point of ice, on heating shows further break down of these bonds. But now the density instead of increasing shows a decrease with the rise of temperature because of the greater kinetic motion of the molecules. Due to this latter effect H_2O molecules move further apart causing expansion in volume or decrease in the density with the rise in temperature.

The effect of temperature on the expansion of water can be breifly summarized on the basis of two opposite effect:

(1) The breaking down of hydrogen bonds which enables water molecules to crowd closer together. This effect predominates at lower temperature upto 3.98°C and the density of water increases.

(2) The increased kinetic energy of water molecules causes them to separate by overcoming the inter molecular attractions. This effect dominates over the first effect at temperatures above 3.98°C and therefore, the density of water decreases.

The high boiling point of water and its large heat of vaporization is also due to the fact that enough energy is required to break the groups of water molecules formed by their association through hydrogen bonding.



Ice Structure

CHEMICAL PROPERTIES OF WATER

1. Stability of water:

Water is a very stable compound and it does not decompose appreciably until at 2700°C. The stability of water is indicative of the strength of polar covalent bond. $\overset{-\delta}{O} — \overset{+\delta}{H_2}$

2. Reaction with metals:

As described in the preparation of hydrogen, very active metals react with cold water to form hydrogen and metallic hydroxide solutions.

$$2Na(s) + 2HOH \quad (l) \longrightarrow 2NaOH\,(aq) + H_2 \quad (g)$$

Less active metals like magnesium, aluminium, zinc and iron react with water at high temperature to liberate hydrogen and form metallic oxides.

3. Reaction with non-metals:

Chlorine reacts with water at ordinary temperature to produce hydrochloric acid and hypochlorous acid.

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

Carbon reacts with steam to form a mixture of carbon monoxide and Hydrogen, known as water gas.

$$C(s) + H_2O(g) \longrightarrow \underbrace{CO(g) + H_2(g)}_{\text{Water gas.}}$$

4. Reactions with Metallic Oxide:

Oxides of many metals are insoluble in water. However, oxides of alkali and alkaline earth metals dissolve in water to form **soluble** hydroxide.

$$Na_2O(s) + HOH(l) \longrightarrow 2NaOH(l)$$

$$CaO(s) + HOH(l) \longrightarrow Ca(OH)_2(l)$$

$Ca(OH)_2$ solution is the lime water used to test the CO_2 gas. Oxides like CaO and Na_2O are known as basic anhydrides or compounds without water which dissolve in water to form a solution containing a base. *A basic anhydride is thus an oxide of a metal which combines with water to form a solution containing a base.*

5. Reaction with Oxides of Non-metals:

The oxides of non-metals generally unite with water to form solutions which contain acids. For example:

$$CO_2(g) + H_2O(l) \longrightarrow \underset{\text{Carbonic Acid.}}{H_2CO_3(aq)}$$

$$P_2O_5(s) + 3H_2O(l) \longrightarrow \underset{\text{Orthophosphoric acid.}}{2H_3PO_4(aq)}$$

Consequently such oxides of non-metals are known as acid anhydrides. *The acidic anhydride is thus an oxide of a non-metal which when unites with water forms a solution containing an acid.*

6. Hydration Reaction:

Many compounds and ions combine with water to form hydrates. The water of hydration is present in definite proportions by weight and the physical properties of the hydrated compounds are different from those of anhydrous substance and water. This suggests that water of hydration is chemically combined. Examples of hydrated substances are:

$$\overset{+}{H} + H_2O \longrightarrow H_3O^+ \text{ (Hydronium ion)}$$

$$CuSO_4 + 5H_2O \longrightarrow CuSO_4.5H_2O \text{(Hydrated copper sulphate)}$$

Other examples of hydrates are $Na_2CO_3 . 10H_2O$ (washing soda) $ZnSO_4 . 7H_2O$ and $CaCl_2 . 6H_2O$.

When water of hydration is present in crystalline compounds it is known as *water of crystallization*. The water of crystallization is usually easily removed on heating the crystals above the boiling point of water.

$$\underset{\substack{\text{Hydrated copper sulphate} \\ \text{(Blue)}}}{CuSO_4 . 5H_2O(s)} \longrightarrow \underset{\substack{\text{Anhydrous copper sulphate} \\ \text{(White)}}}{CuSO_4 + 5H_2O(g)}$$

Some crystalline hydrates, such as $Na_2CO_3 . 10H_2O$ when exposed to the air lose some or all molecules of water of crystallization. This property is known as efflorescence. The efflorescence occurs when the aqueous vapour pressure of the hydrate is greater than the vapour pressure of the surrounding air.

On the other hand there are certain substances which absorb water from the air to form a solution. 'This property is known as deliquescence $CaCl_2$, $MgCl_2$ and glycerol are deliquescent. The deliquescent substances have low aqueous vapour pressure as compared to the vapour pressure in the air and therefore, absorb moisture from the atmosphere.

Many substances such as silk, wool, hair and tobacco take up small amount of water from the air and therefore only get moist. Hence a general term *hygroscopic* is used to represent the substances which absorb moisture from the air. The *hygroscopic materials which form solution are called deliquescent substances.* The common table salt is hygroscopic because it contains a small amount $MgCl_2$, a very deliquescent substance.

7. Hydrolysis Reactions:

In general, normal salts, such as NaCl and KNO_3, when dissolved in water give neutral solutions. However, in some cases salt solutions are not neutral but either acidic or alkaline. Such salts are said to hydrolyse in water solution. Hydrolysis *is an acid base reaction between water and an ion of a dissolved salt.* The water acts as an acid or base depending upon the nature of the ion of the dissolved salt.

There are two general types of hydrolysis reactions.

1. Hydrolysis due to Reaction between as anion base and water:

Anions like CO_3^{--}, CH_3COO^-, that are conjugate bases of weak acids, may act like proton acceptors in water solution. Water molecules behave like proton donors or acids. The net result is an increase in the OH ion concentration of the solution making it alkaline.

For example when the salt sodium carbonate is dissolved in water, the base CO_3^{--} ion accepts a proton from water molecule to form the slightly ionized bicarbonate ion HCO_3^- and OH^- ion.

$$\begin{array}{ccccccc} CO_3^{--} & + & H_2O & \rightleftharpoons & HCO_3^- & + & OH^- \\ (\textit{Base}) & & (\textit{Acid}) & & \text{Conjugate} & & \text{Conjugate} \\ & & & & \text{acid} & & \text{base} \end{array}$$

The sodium ion Na^+ remains inert and does not react with water. Thus the concentration of OH^- builds up until equilibrium is reached. The concentration of hydrogen ion H^+ in solution is less as the former is removed to form HCO_3^- ion. Thus the pH is greater than 7 and the solution is alkaline. In general the salts of a strong base and a weak acid hydrolyse in water to form alkaline solutions Sodium acetate in water also gives an alkaline solution.

$$\begin{array}{ccccccc} CH_3CO\bar{O} & + & HOH & \rightleftharpoons & CH_3COOH & + & O\bar{H} \\ \text{Base} & & \text{Acid} & & \text{Conjugate} & & \text{Conjugate} \\ & & & & \text{Acid,} & & \text{Base} \end{array}$$

2. Hydrolysis due to reaction between a cation acid and water.

Cations having hydrogen, such as $\overset{+}{NH_4}$ and hydrated cation like $[Cu(H_2O)_4]^{+2}$ may act like proton donors in water solution. Water molecules are proton acceptors or base. The net effect is an increase in the hydronium ion, H_3O^+ concentration of the solution making it acidic.

A water solution of ammonium chloride NH_4Cl is acidic. This is because NH_4^+ ions donate protons to water molecules.

$$\underset{\text{Acid}}{\overset{+}{NH_4}} \quad + \quad \underset{\text{Base}}{H_2O} \quad \rightleftharpoons \quad \underset{\substack{\text{Conjugate}\\\text{Base}}}{NH_3} \quad + \quad \underset{\text{Conjugate Acid}}{\overset{+}{H_3O}}$$

The concentration of $H_3\overset{+}{O}$ builds up until equilibrium is established. The pH is less than 7 and the solution is acidic.

Hydrate cupric ion $[Cu(H_2O)_4]^{+2}$, in solution undergoes hydrolysis to form acidic solution.

$$[Cu(H_2O)_4^{+2}] \quad + \quad H_2O \longrightarrow [Cu(H_2O)_3\overset{+}{OH}] + H_3\overset{+}{O}$$

This explains the acidic nature of cupric salts solution. In general salts of a weak base and strong acid hydrolyse in water to form acidic solution.

Salts of weak base and weak acids, such as ammonium acetate, on hydrolysis produce equal amount of H_3O^+ and OH^- ions and hence their aqueous solution is neutral.

(i) $\underset{\text{Ammonium Acetate}}{CH_3COONH_4} \rightleftharpoons \overset{+}{NH_4} + CH_3CO\bar{O}$

(ii) $\overset{+}{NH_4} + H_2O \rightleftharpoons NH_3 + H_3\overset{+}{O}$

(iii) $CH_3CO\bar{O} + H_2O \rightleftharpoons CH_3COOH + O\bar{H}$

Salts of strong acids and strong bases will get completely ionized in aqueous solution without disturbing the concentration of H^+ or OH^- ion and thus the resulting solution will be neutral.

Ionization of water:

Under hydrolysis we have read that water can act as a proton donor to basic anions like CO_3^{--} and CH_3COO^- ions. This property of water molecules can be explained on the basis of the weak ionization of water.

$$H_2O\,(l) \rightleftharpoons (\overset{+}{H}\,(aq) + \overset{-}{OH}\,(aq)$$

The concentration of ions is very low and for this reason pure water is ordinarily considered as non-conductor of electricity. In fact water is a weak electrolyte.

The equilibrium of the ionization of water can be represented as:

$$K = \frac{[H^+]\,[\overset{-}{OH}]}{[H_2O]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The concentration of unionized water as compared to the ions is so large (55.5 M/litre) that it is virtually constant. Equation (1) is rearranged to give

$$K\,[H_2O] = [H^+]\,[\overset{-}{OH}]$$

$$K_w = [H^+]\,[OH]^- \quad \text{where } K_w = K \times [H_2O] \ldots\ldots\ldots (2)$$

K_w is known as the ion product of water and indicates that in any aqueous solution both hydrogen and hydroxyl ions must be present and that always the product of the concentration of the two ions is constant. The value of K_w varies with the temperature. It increases with rise in temperature. At 25°C its value is $K_w = 1 \times 10^{-14}$.

Substituting the value of K_w in equation (2)

$$K_w = [H^+]\,[\overset{-}{OH}] = 1 \times 10^{-14} \ldots\ldots\ldots\ldots\ldots (3)$$

According to equation (1) the concentration of H^+ and OH^- of pure water is equal, i.e.

$$[OH^-] = [H^+]$$

Equation (3) becomes

$$[H^+] \times [H^+] = [H^+]^2 = K_w = 1 \times 10^{-14}$$

$$\text{or} \quad [H^+] = \sqrt{K_w} = \sqrt{1.00 \times 10^{-14}} = 1 \times 10^{-7}\,M$$

$$[OH^-] = [H^+] = 1 \times 10^{-7}\,M$$

The pH of Solution.

The acidity or alkalinity of solutions can be measured in terms of H^+ ion concentration only, because in any solution the ionic product H^+ and OH^- ion is constant. One convenient method of expressing H^+ ions concentration is the use of pH scale. The pH of any solution is defined:

$$pH \equiv \log \frac{1}{[H^+]}$$

$$\text{or} \quad pH = -\log [H^+]$$

For example the pH of water at 25°C is equal to

$$pH = \log \frac{1}{10^{-7}} = \log 10^7 = 7$$

$$\text{or} \quad pH = -\log 10^{-7} = 7$$

If the pH of a solution is known we can calculate its $[H^+]$ concentration.

$$[H^+] = 10^{-pH}$$

Thus for a solution of pH = 4, $[H^+] = 10^{-4}$

Similarly for a solution of pH = 13, $[H^+] = 10^{-13}$

The range of pH values usually falls between 0 and 14. The pH = 7 corresponds to a neutral solution while the values of pH greater than 7 indicate an alkaline solution, and solutions with lower pH than 7 are acidic in nature.

Water as a Solvent.

Water is a universal solvent for many inorganic and certain organic compounds. This characteristic property of water that it dissolves more or less of everything is due to the following two reasons :

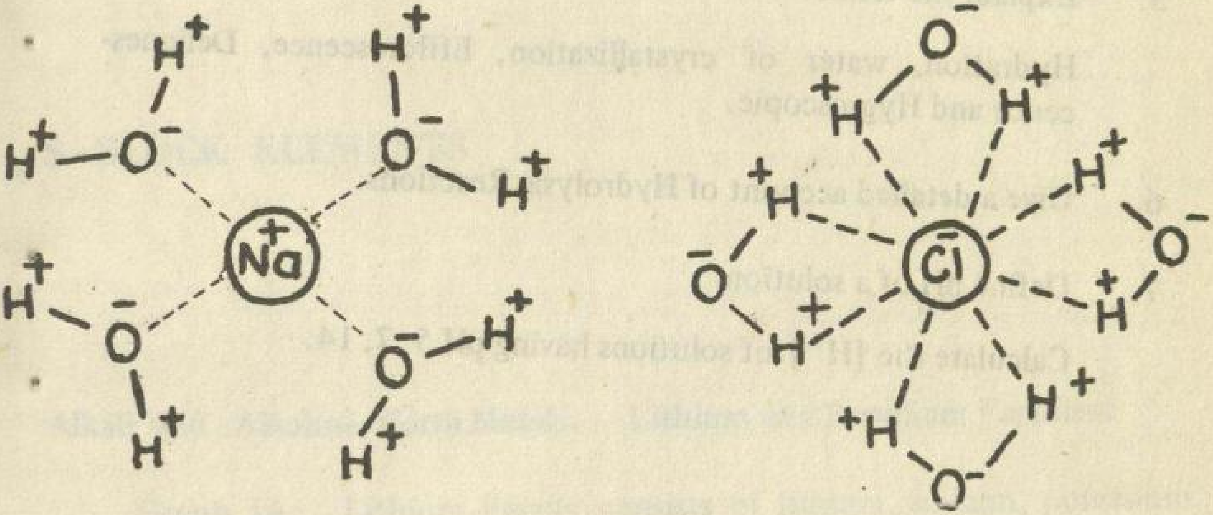
1. **Dielectric constant.** Coulmb's Law states that the force of attraction between two oppositely charged electrical bodies is directly proportional to the product of the charge and inversely proportional to the square of the distance.

Mathmatically: Force $\propto \frac{(X)(Y)}{r^2}$ where X and Y are two opposite charges and r is the distance between them or Force = $\frac{(X)(Y)}{D\ r^2}$ where D, the proportionality constant is called dielectric constant of the medium in which the charged bodies are lying. The above equation tells us that the greater is the value of D the smaller the value of the force of attraction between the charges and the smaller the value of D the greater the foroe of attraction. Thus it will be easier to separate two charges from one another in a liquid having a high dielectric constant. Water has got a high dielectric constant of 80 at 18°C. The high value of dielectric constant reduces the attraction between two oppositely charged bodies. Thus the cations and anions of a salt dissolved in water will have less force of attraction than that in vacuum facilitating its solution. The value of dielectric constant for petrol is 2.1 and 20 for ethanol. As compared to water it will be comparatively difficult to separate two charges placed in either of the two liquids as compared to water. Thus is seems that a high dielectric constant is a necessary attribute for a good solvent for ionic compounds and polar molecules of organic nature.

2. **Polarity.** The second reason for water's distinct ability to act as solvent for ionic compounds is its highly polar nature. The interaction between the ion and the dipolar water molecule is called hydration as already discussed earlier in this chapter. The negative polar end of water attracts the

positive ion and the positive pole of water holds the negative ion. The ions are thus surrounded by water molecules and the dipolar attraction of water molecules is sufficient to release these ions from their fixed positions in the crystals.

Fig. 3.2. . . . . shows the solution of NaCl in water.



It may be pointed out that when we say Barium Sulphate, $BaSO_4$ is insoluble in water we mean that the Ba^{++} and SO_4^{--} ions in a crystal lattice are held together by enough strong electrostatic force that these ions cannot be pulled away from their crystal lattice positions by the dipolar molecules of water.

QUESTIONS

1. Explain the unusual behaviour of water towards temperature changes. Why is ice lighter than water at 0°C ?

2. (a) How would you explain the bursting of water supply pipes on hill stations like Nathiagali and Murree during the winter.

   (b) Why do the fish remain alive in water under the frozen lake during severe winter ?

3. What is a hydrogen bond ? Discuss its significance in determining the physical properties of water.

4. What do you understand by Acidic and Basic anhydrides ? Give examples.

5. Explain the terms:

   Hydration, water of crystallization, Efflorescence, Deliquescence and Hygroscopic.

6. Give a detailed account of Hydrolysis Reactions.

7. Define pH of a solution.

   Calculate the $[H^+]$ of solutions having pH 5, 7, 14.

CHAPTER 4

S–BLOCK ELEMENTS

Alkali and Alkaline Earth Metals: Lithium and Beryllium Families:

Group IA: Lithium Family consists of lithium, sodium, potassium, rubidium, cesium and francium. They all have one electron in the outermost shell; so are univalent metals.

Element	Symbol	At. No.	Electronic configuration	Oxidation state
Lithium	Li	3	[He] . $2S^1$	+ 1
Sodium	Na	11	[Ne] . $3S^1$	+ 1
Potassium	K	19	[Ar] . $4S^1$	+ 1
Rubidium	Rb	37	[Kr] . $5S^1$	+ 1
Cesium	Cs	55	[Xe] . $6S^1$	+ 1
Francium	Fr	87	[Rn] . $7S^1$	+ 1

Because of similarities in the electronic structure of these elements, many similarities in chemical behaviour could be expected. They all form alkaline oxides and Hydroxides. That is why they are also known as Alkali Metals:

Besides, they are all soft, highly reactive metals, forming colourless ionic compounds.

(1) General Properties

(1) These elements have the largest size in their respective period hence have low density.

(2) When the outer electron is removed to give a positive ion, the size of the ion shrinks. The positive charge on the nucleus becomes greater than the number of electrons, so the electrons are attracted towards the nucleus and the ion become smaller than the original atom.

(3) As we go down the group, the size of the atoms and ions increases from Li to Fr, because of the extra shells of the electrons that are added.

(4) As the outer orbital electrons are a long way from the nucleus, they are relatively easy to remove hence their ionisation potential is low, which decreases, as the size of the atom increases from Li to Fr.

Symbol	Density at 20°C	Atomic Radius A°	Ionic Radius A°	Ionisation Energy K. Cal/mole	Electro-negativity.	M.P. °C	B.P. °C
Li	0.53	1.23	0.68	124	1.0	186	1372
Na	0.97	1.57	0.98	118	0.9	98	893
K	0.80	2.03	1.33	100	0.8	63	774
Rb	1.53	2.16	1.48	96	0.8	39	700
Cs	1.87	2.35	1.67	90	0.7	29	670
Fr	—	—	—	—	—	—	—

(5) The electronegativity values of elements in this group are very small so that when these elements react with other elements to form compounds, a large electronegativity difference is possible and ionic compounds are formed. This may also mean weaker interaction among the metal atoms in the crystal lattice. Hence these metals can be cut with a knife; degree of softness increases as we go down the group.

(6) Their M.P, and B.P. are low and decrease as the size increases. M.P. of lithium is rather high (In general the first element in each group differs appreciably from the rest of the group).

(7) The alkali elements crystallise to give a body centered cubic lattice in which the lattice points are occupied by + 1 ions. The metal ions have inert gas configuration, have no unpaired electrons and are diamagnetic and colourless.

Peculiarities of Lithium

Diagonal relationship :

Li differs from the rest of the elements of group IA for example :

1. M.P. and B.P. of Li are comparatively high.
2. Li is much harder than the other group IA metals.
3. Li reacts least readily with O_2 forming the normal oxide, higher oxides being unstable.
4. When exposed to the air it forms nitride.
5. Li is much less electropositive, therefore many of its ionic compounds are less stable as Li_2CO_3 , $Li(NO_3)$, $Li\ (OH)$ are all changed to oxide on gentle heating and no solid bi-carbonate is known.
6. The Li^+ ion and its compounds are more heavily hydrated than those of the rest of the group.

On the other hand, Li shows slight similarities with group IIA elements, rticularly Mg. This is due to the polarising power, *ionic charge/ionic radius* ing similar for these two elements. Some points of similarity are :

1. Unlike group I, but like group II, Li forms nitride.

2. Like corresponding Mg salts Li_2CO_3, Li_3PO_4 & LiF are insoluble and Li (OH) is only sparingly soluble in water.

3. Due to their covalent nature, the halides and alkyls of Li an Mg are soluble in organic solvents. This resemblance in properties betwee Li and Mg is called Diagonal relationship in which first member of a grou resembles with the 2nd members of the following group. This is also foun between Be and Al and B and Si.

Occurrence:

Sodium and Potassium occur in nature in abundance as salts containin positive monovalent metal ions. Sodium occurs as sodium chloride in sal mines and in sea water. Sodium also occurs in nature as part of some mineral (such as zeolites; sodium aluminium silicates), and as sodium nitrate. Potassium is found in nature as potassium chloride and as a double salt, KCl, $MgCl_2$ $6H_2O$ (Carnalite). Lithium, rubedium and cesium are comparatively rare Francium is radio-active and has a short half life.

Preparation:

Metals of this group are strongest reducing agents known, so they aı not prepared by reducing their oxides. Since the metals are so reactive, the react with water, hence electrolysis of aqueous solution in order to obtain tl metal also does not work, unless Mercury Cathode is used with which tl metal forms an amalgam. But the recovery of pure metal from the amalga is difficult. They can, however, be isolated, by electrolysis of fused hali with some other salt added to lower the melting point. Thus sodium is ma by the **Downs'** process (Electrolysis of NaCl with $CaCl_2$) or by Castner p cess, using fused NaOH.

$$\begin{array}{lcccl} \underset{\text{Fused}}{2NaCl} \xrightarrow{\text{Electrolysis}} & 2Na^+ & + & 2\bar{Cl} & \text{(Down's process)} \\ & \downarrow & & \downarrow & \\ & \underset{\text{Cathode}}{2Na} & & \underset{\text{Anode}}{Cl_2} & \end{array}$$

$$\begin{array}{llcl} 2NaOH \xrightarrow{\text{Electrolysis}} & \overset{+}{2Na} & + & \overset{-}{2OH} \text{ (Castner Process)} \\ & \downarrow & & \downarrow \\ & 2Na & & 2OH \rightarrow H_2O + \frac{1}{2}O_2 \\ & \text{(Cathode)} & & \text{(Anode)} \end{array}$$

Chemical Properties of the Metals and their Compounds:

These elements being very reactive tarnish very rapidly in air to form xides. Li also forms nitride. Reaction with water, as referred earlier, increa- s in violence on descending from Li to Cs, librating hydrogen and forming droxides.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

Oxides are formed when the metals are burnt in air; lithium forms the onoxide (Li_2O), sodium peroxide (Na_2O_2) and the others form super xide of the type MO_2.

The monoxide is ionic ($2\overset{+}{Li}$ and O^{2-}), the peroxides contain $-O-O-)^{2-}$ and the super oxides have a three electron bond $(O-O)^{-}$ hich makes it paramagnetic and coloured. The typical oxides M_2O are rongly basic except Li_2O. They are all soluble in water and thermally able illustrating the strong electropositive nature of the metal. The per- ides and superoxides are oxidising agents and react with water and acid ing H_2O_2 and O_2.

$$Na_2O_2 + 2H_2O \longrightarrow H_2O_2 + 2NaOH$$

All the simple salts of this group are soluble in water and are decom- ed by passage of electricity. Because of the highly electropositive or basic ure of these elements, their compounds are quite stable, except for Li. eir carbonates are stable to heat. Their bicarbonates are, however, conver- to carbonates by gentle heat. LiCl, NaCl, KCl all have face centred cubic stals, but as the size of the metal ion increases it becomes possible to more halogen ions around the metals. So Rb, Cs may have either NaCl e structure or B.C.C. structure like that of CsCl.

Uses:

(1) Though all the alkali metals are good reducing agents, only Na finds extensive use for this purpose. It is used to make other metals by reducing their chlorides.

(2) Cesium being the metal from which electrons are ejected easily by light (photo electric effect), so finds use in photocells, a device for converting light signals to electric signals.

Sodium hydroxide, NaOH:

It is mostly prepared commerically as a by-product in the electrolysis of brine (saturated solution of common salt), see under the preparation of chlorine (chapter 9)

The cell reaction for the electrolysis of Brine solution is:

$$\begin{tikzcd}
\underset{\text{(Solution)}}{2NaCl} & \overset{\text{Electrolysis}}{\leftrightarrows} & 2Na^{+} \arrow[d] & + & 2Cl^{-} \arrow[dd] \\
& & 2Na \arrow[d, "+ 2H_2O"] & & \\
& & \underset{\text{(cathode)}}{2NaOH + H_2(g)} & & \underset{\text{(Anode)}}{Cl_2(g)}
\end{tikzcd}$$

In small amounts it can also be made by adding calcium hydroxi (slaked lime) to a sodium carbonate solution.

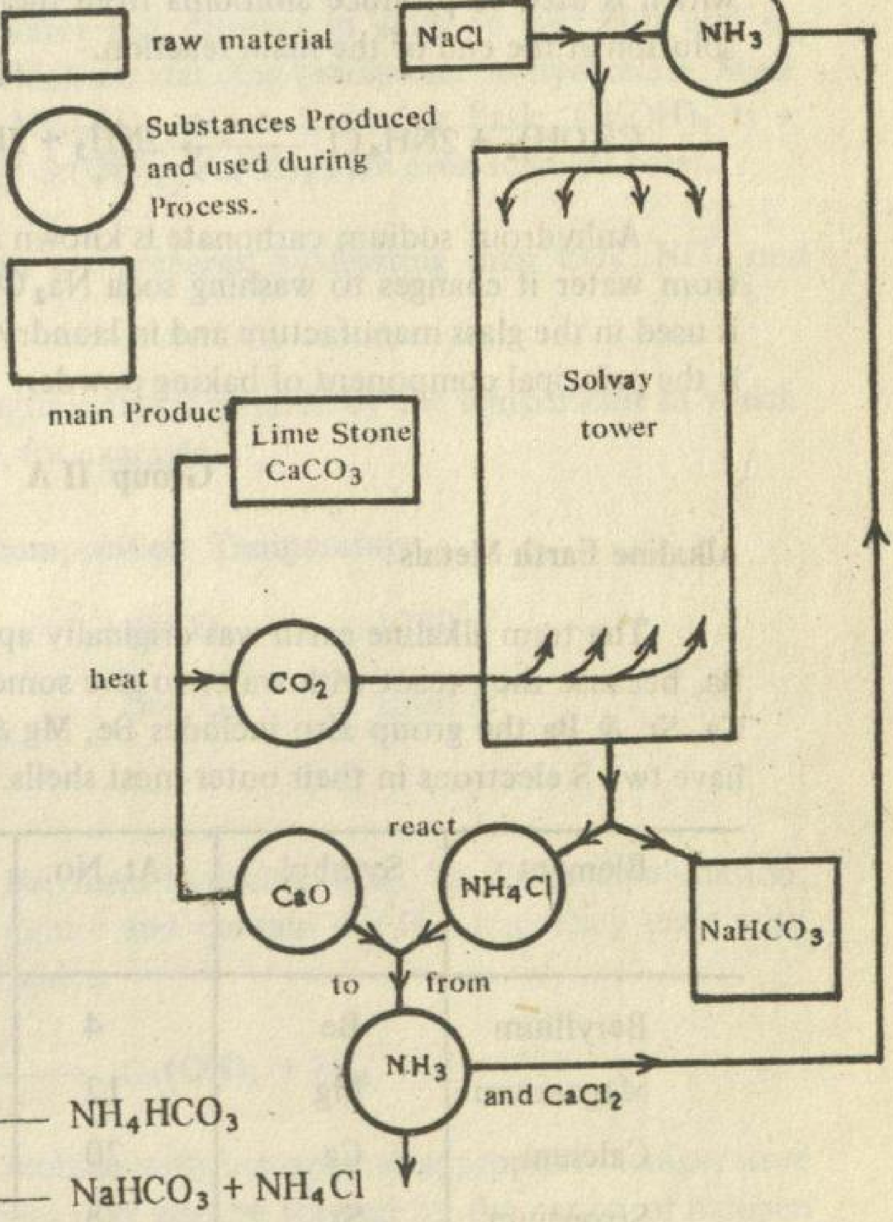
$$Na_2CO_3 + Ca(OH)_2 \longrightarrow \underset{\text{(solution)}}{2NaOH} + CaCO_3 \downarrow$$

The precipitated $CaCO_3$ is filtered off, and the solution of NaOH concentrated by evaporation.

Sodium hydroxide is a white crystalline solid and a very caustic sub tance, because of its destructive effect on skin, hair and wool. It is deliqu cent and combines with CO_2 of the air to form Na_2CO_3. Its aqueous solution is basic. It reacts with fats to form soap and glycerol. Hence it is used in soap making. It is also used in the production of rayon, paper and cellulose film.

Sodium Carbonate:

It is another commercially important compound of sodium. It is prepared by the SOLVAY PROCESS, developed by Ernest Solvay, a Belgian in 1864.


raw material
Substances Produced and used during Process.
main Product
NaCl
NH$_3$
Solvay tower
Lime Stone CaCO$_3$
heat
CO$_2$
react
CaO
NH$_4$Cl
NaHCO$_3$
to
from
NH$_3$
and CaCl$_2$

The raw materials for the Solvay Process are NH_3, CO_2 and NaCl. The cold saturated solution of NaCl is further saturated with NH_3 and CO_2.

The stages in the solvary process are shown in Figure. For the main reactions, brine (conc. NaCl solution) saturated with ammonia is passed down a tower and carbon dioxide is forced up the tower. The equations for this reaction can be written as:

) $H_2O + CO_2 + NH_3$ —— NH_4HCO_3

i) $NH_4HCO_3 + NaCl$ —— $NaHCO_3 + NH_4Cl$

The solution is cooled to 15°C, whereby sodium bicarbonate whic is least soluble under these conditions, is precipitated. $NaHCO_3$ is filter out and heated to get anhydrous Na_2CO_3.

$$2NaHCO_3 \xrightarrow{\text{heat}} \underset{\text{(Soda ash)}}{Na_2CO_3} + H_2O + CO_2$$

The carbon dioxide required for the process is made by heating lim stone. The calcium oxide is reacted with water to form calcium hydroxi which is used to produce ammonia from the ammonium chloride left in t solution at the end of the main reaction.

$$Ca(OH)_2 + 2NH_4Cl \longrightarrow 2NH_3 + 2H_2O + CaCl_2$$

Anhydrous sodium carbonate is known as soda ash. When recrystallize from water it changes to washing soda $Na_2CO_3 . 10H_2O$. Sodium carbona is used in the glass manufacture and in laundry. Sodium bicarbonate, NaHC is the principal component of baking powder.

Group II A

Alkaline Earth Metals:

The term alkaline earth was originally applied to the oxides of Ca, Sr, Ba, because they react with water to give somewhat alkaline solution. Besid Ca, Sr, & Ba the group also includes Be, Mg & Radium. Metals in this gro have two S electrons in their outer-most shells.

Element	Symbol	At. No.	Electronic configuration	Oxidatio state
Beryllium	Be	4	$[He]\ 2S^2$	+ 2
Magnesium	Mg	12	$[Ne]\ 3S^2$	+ 2
Calcium	Ca	20	$[Ar]\ 4S^2$	+ 2
Strontium	Sr	38	$[Kr]\ 5S^2$	+ 2
Barium	Ba	56	$[Xe]\ 6S^2$	+ 2
Radium	Ra	88	$[Rn]\ 7S^2$	+ 2

General Properties of the Metals and their Compounds:

(1) Elements of group II A are less electropositive than elements of group I, but still react with water to form H_2 and the metal hydroxide. Magnesium decomposes hot water while the other elements react with cold water. $Be(OH)_2$ is amphoteric; the other hydroxides increase in basic strength.

(2) As their atoms get larger their ionization potential decreases.

(3) Elements of group II burn in oxygen to form ionic oxide MO. Of these BeO is insoluble in water but dissoves in acids to give salts and in alkalies to give beryllates, which on standing precipitate to hydroxide. MgO reacts with water forming $Mg(OH)_2$ which is weakly basic, $Ca(OH)_2$ is a moderately strong base, while $Sr(OH)_2$, $Ba(OH_2)$ are even stronger bases.

Oxides of the elements are prepared by heating their CO_3''. NO_3' and OH'.

Increase in basic strength is also illustrated by the temperature at which their carbonates decompose, for example.

Decomposition Temperature

$BeCO_3$	100°C	$SrCO_3$	1290°C
$MgCO_3$	540°C	$BaCO_3$	1360°C
$CaCO_3$	900°C		

All elements except Be, form hydrides MH_2, by direct combination. The hydrides are ionic in nature and contain the H^- ion. They react with water to form H_2 and hydroxides.

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$$

(4) These metals combine with halogens at appropriate temperature forming halides, MX_2. Halides may also be formed by the action of halogen acids on the metals or their carbonates. Beryllium halides are covalent,

hygroscopic and fume in air due to hydrolysis. The other metals halides are, however ionic and readily soluble in water. Their solubility decreases somewhat with increasing atomic weights. Of course fluorides of these metals are all insoluble. Halides are hygroscopic and form hydrates. $CaCl_2$ is a well known drying agent.

(5) In contrast to group I A, alkaline earth elements burn in nitrogen to form nitrides, M_3N_2. They are all colourless, crystalline solides, and react with water to liberate NH_3 at the same time forming metal oxides, or hydroxide:–

$$M_3N_2 + 6H_2O \longrightarrow 3M(OH)_2 + 2NH_3$$

(6) Heating the metals or their oxides with carbon, yields carbides, MC_2. CaC_2 is the best known carbide. It reacts with water to liberate acetylene.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2 \uparrow$$

(7) The metals liberate hydrogen from acids, although Be reacts slowly.

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2$$

(8) Most of the salts are soluble. Sulphates of **Ca, Sr & Ba** are insoluble, while the carbonates, oxalates chromates and fluorides of the whole group are insoluble. This fact forms the basis of qualitative test of these elements.

Occurrence:–

Be is rather rare, and occurs mostly as aluminium Beryllium silicate ($Be_3 Al_2 Si_6O_{18}$) called Beryl. Mg is found as Mg^{+2} ion in salt deposits, particularly as slightly soluble carbonate and also in sea water. Calcium is found in lime stone, $CaCO_3$, and gypsum, $CaSO_4.2H_2O$. Bones also have $Ca_3(PO_4)_2$. Sr is rather rare and found principally as $SrCO_3$. Ba occurs as $Ba SO_4$. Radium is radio-active and extremely rare and occurs in trace amounts (one part in 10^{12}) in ores such as pitch blende (U_3O_8).

The physical data for the elements of this group is given in the table below:–

Element	Density	At. radius A°	Ionic radius A°	Ionization energy K Cal/mole		Electronegativity	ΔH sub. K cal/mole	M.P. °C	B.P. °C
				Ist	2nd				
Be	1.8	0.89	0.31	214	429	1.5	77.9	1283	2780
Mg	1.7	1.36	0.65	175	345	1.2	35.6	656	1106
Ca	1.6	1.74	0.99	140	274	1.0	42.2	850	1487
Sr	2.6	1.91	1.13	132	253	1.0	39.1	770	1383
Ba	3.5	1.98	1.35	120	230	0.9	42.5	710	1638
Ra	5.0	–	1.50	–	–	–	–	–	–

Extraction of the Metals:–

Metals of this group are not easy to produce by chemical reduction, because they are strong reducing agents and will form carbides. They are strongly electropositive, so their aqueous solution cannot be used for displacing one metal by the other or for electrolysis, because the metal reacts with water.

Electrolysis of fused metal halides is generally used for the preparation of these metals.

Be metal is usually prepared by the electrolysis of a molten mixture of $BeCl_2$ and NaCl. Beryllium compounds are used as phosphor in some fluorescent light tubes. Beryllium bronze, an alloy with copper has great tensile strength and can be hardened by heat treatment. Be is also used to some extent in the window of X-ray tubes. Beryllium and its compounds are extremely poisonous.

Magnesium, an important structural metal, is a constituent of many alloys. It was formerly prepared by heating MgO with carbon at 2000°C and shock cooling the gas to avoid a state of equilibrium.

$$MgO + C \rightarrow Mg + CO \uparrow$$

Magnesium is commercially obtained by the electrolysis of fused magnesium chloride, $MgCl_2$, obtainable from sea water.

$$MgCl_2 \xrightarrow{\text{Electrolysis}} \underset{\text{(Cathode)}}{Mg} \quad + \quad \underset{\text{(Anode)}}{Cl_2}$$

Calcium, Strontium and Barium can also be obtained by the electrolysis of the respective chlorides. Mg flame is brilliant and rich in ultraviolet rays. It is used in flashlight powders, military flares and incendiary bombs.

Diagonal Relationship and Peculiarities of Be :–

Beryllium resembles Aluminum of group III A in many respects:

1. Be atom is very small and has a high charge density, so has a high tendency to covalency. Thus the M.P. of its compounds is lower ($BeFe_2$ –M.P. 800°C for rest of the metals almost 1300°C). These compounds are soluble in organic solvents and hydrolyse in water like the compounds of Aluminium.

2. Be forms many complexes not typical of Group IA & IIA'

3. Be like Al is rendered passive by HNO_3.

4. Be like Al is amphoteric liberating H_2 with NaOH.

5. Be_2C, like Al_4C_3 yields methane on hydrolysis.

QUESTIONS

1. Explain why:

   (i) Sodium form + 1 ion.

   (ii) M.P., B.P. and hardness of the element of group IA decrease down the group.

   (iii) Li^+ has much higher value of heat of Hydration than Cs^+.

   (iv) Substances which are good electric conductors are good heat conductors too.

   (v) Oxidation potential as well as ionization potential of Li are highest in the group.

2. In what respect is Beryllium more similar to Aluminum than to the members of its own family.

3. Compare the members of the Li family with those of Beryllium family with regards to their (1) Electronic configuration (2) Atomic radius (3) Ionization energy etc.

4. On the basis of electronic configuration and the position in the periodic table, answer the following questions:

   (i) Is calcium likely to be a metal or non-metal.

   (ii) Is calcium likely to resemble Mg or K in its chemistry.

   (iii) Is Ca likely to have a higher or a lower B.P. than K? than Sr ?

5. From ionizing energies predict which solid substances involve bond having the most ionic character, $BeCl_2$, $MgCl_2$, $SrCl_2$. Which substance is expected to have most covalent character in its bonds.

6. Compare a typical alkali element with an alkaline earth element with respect to ionization potential, ionic size, M.P. and hardness. Account for similarities and differences.

7. Why are gorup IA elements (a) Univalent (b) largely ionic (c) strong reducing agents (d) poor complexing agents (e) why have they lowest I.P. in their periods.

8. Why and in what ways does Li resemble group IIA metals.

9. What chemicals are obtained on the large scale from NaCl. Outline the process.

10. How are group I & II elements obtained and why are usual methods of extraction not suitable?

CHAPTER 5

BORON AND ALUMINIUM

Group III A:

This group consists of Boron, Aluminium, Gallium, Indium, and Thallium. They all have three electrons in the valency shell.

Element	Symbol	At. No.	Electronic Configuration	Oxidation State
Boron	B	5	$[He]\,2S^2\,2p^1$	+ 3
Aluminium	Al	13	$[Ne]\,3S^2\,3p^1$	+ 3, + 1
Gallium	Ga	31	$[Ar]\,3d^{10}\,4S^2, 4p^1$	+ 3, + 1
Indium	In	49	$[Kr]\,4d^{10}\,5S^2\,.5p^1$	+ 3, + 1
Thallium	TI	81	$[Xe]\,4f^{14}\,5d^{10}.\,6S^2\,6p^1.$	+ 3, + 1

General Properties:

Boron is a non-metal, other elements in this group are fairly reactive metals. Aluminium is the third most abundant element in the earth crust and is the most abundant metal. But the other elements are less common.

All these elements show an oxidation state + 3. The small size of the ions, their high charge and the large values of the sum of their ionization potential suggests that elements are largely covalent in their compounds. Boron is always covalent. Simple compounds of the other elements such as $AlCl_3$, $GaCl_3$ are covalent when anhydrous. However, in solution large amount of hydration energy evolved, offsets the high ionization potential and the metal ions exist in hydrated state. Some of the elements of this group show lower valency state in addition to the normal valency of 3. In fact the univalent Thallium (Thallous) compounds are the most stable. Monovalency is expalined by the S electrons in the outer shell remaining paired and not participating in bonding, because the energy to unpair them is very great. This occurs particularly among heavy elements in the P–Block and is called the Inert pair effect. Gallium is apparently divalent in a few compounds such as Gallium di-chloride, $GaCl_2$ but its structure has been shown as $Ga^+[GaCl_4]^-$ which contains Ga^+ and Ga^{+3} ions.

Finely divided amorphous Boron is usually impure and burns in air to form the oxide and nitride and in halogens to form trihalides. It reduces HNO_3 and H_2SO_4, and liberates hydrogen with NaOH. Pure crystalline Boron on the other hand, is unreactive, except at very high temperature or with reagents such as hot conc, H_2SO_4 or Na_2O_2.

Symbol	At. Radius A°	Ionic Radius	Electro negativity	M.P. °C	B.P. °C
B	0.80	0.20	2.0	2300	2550
Al	1.25	0.52	1.5	658	1800
Ga	1.25	0.80	1.6	29.75	1700
In	1.50	0.81	1.7	155	1450
TI	1.55	0.95	1.8	303.5	1650

The metals Al, Ga, In, Tl are silvery white. Al is stable in air, as it develops an oxide film, which protects the metal from further attack. If the oxide covering is removed, the metal is rapidly oxidised and decomposes cold water.

Ga and In are stable in air and are not attacked by water, except when free oxygen is present. Thallium is a little more reactive and is superficially oxidised in air.

Electropositive Character:

The electropsoitive nature of the element increases from Boron to Thallium. Boron forms acidic oxides and hydroxides.

Aluminium and gallium form amphoteric oxides and hydroxides. The oxides and hydroxides of indium and thallium are basic. Thus the acidic or non-metallic character decreases going down the group. This trend in the variation of electro-positive character can be explained on the basis of increase in the size of M^{+3} ions with increase in atomic number.

Peculiarity in the properties of Boron:

Like Li and Be, Boron has electronic structure in which the valency electrons are shielded from the nucleus only by K shell. This gives Boron a higher ionization potential than Al, Ga, In, and Tl, Because of this high ionization potential Boron is less metallic than other elements of this group. Boron is actually a non-metal with a trace of metallic character.

Extraction of elements:

Boron is obtained by reduction of B_2O_3 with Mg or Na or by using a tungsston filament in the reduction of BCl_3 with H_2. Very pure Boron is obtained by the pyrolysis of BI_3 and is used to increase the harden ability of steel. Boric acid and Boron have extensive applications.

Aluminium is the third most abundant element in the earth's crust (about 7.5%). It does not occur in the free state. In combined form it is found in a variety of minerals like clays and soils. Its important ores are bauxite ($Al_2O_3 . 2H_2O$) and cryolite (Na_3AlF_6).

The main ore of aluminium is bauxite, which is principally aluminium oxide together with silica and oxides of iron, both of which must be removed. This is conveniently done by using the amphoteric nature of aluminium oxide. The crude ore is treated with hot concentrated sodium hydroxide which dissolves the aluminium oxide as sodium aluminate:

$$Al_2O_3 . 2H_2O + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

The impurities are filtered off and on cooling the solution of sodium aluminate and 'seeding' with a little aluminium hydroxide, the aluminate precipitates as aluminium hydroxide:

$$NaAlO_2 + H_2O \longrightarrow Al(OH)_3 + NaOH$$

The precipitate of aluminium hydroxide is separated and then roasted to form very pure aluminium oxide:

$$2Al(OH)_3 \xrightarrow{1200^\circ C} Al_2O_3 + 3H_2O$$

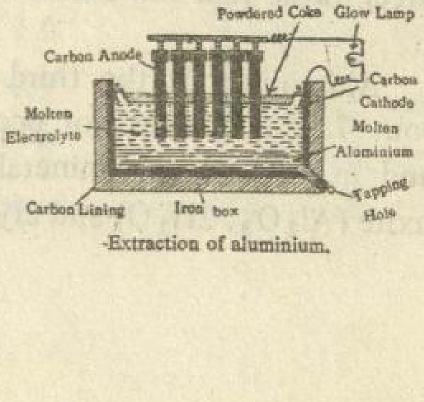
Aluminium oxide has a very high melting point and is almost a non-conductor when molten. Thus it is dissolved in molten cryolite (sodium aluminium fluoride, Na_3AlF_6) which, in addition to lowering the melting point of the aluminium oxide, is an electrolyte.

The molten mixture is electrolysed in a steel tank lined with graphite which serves as cathode. The anodes made up of graphite rods are suspended in molten solution. The electrolysis is carried out at a temperature of 900–1000°C. During the process of electrolysis some AlF_3 is considered to be formed from the solution of Al_2O_3 in fused cryolite, Na_3AlF_6. This on electrolysis yields aluminium metal at the cathode, in molten state which collects at the bottom of the cell. The oxygen reacts with the graphite anode of the cell to form CO_2. The over all reaction may be represented as follows:

$$2Al_2O_3 \overset{900-1000^\circ C}{\rightleftharpoons} 4Al^{+3} + 6O^{-2}$$

$$4Al^{+3} \downarrow 4Al \text{ (cathode)}$$

$$6O^{-2} \downarrow 3O_2 + 3C \downarrow 3CO_2 \text{ (Anode)}$$



Extraction of aluminium.

Aluminium thus obtained is 99% pure,it can be further purified electrolytically.

Properties:

Aluminium is an extremely light, silvery white, soft and weak metal. The pure metal is an excellent conductor of heat and electricity.

Although the metal is very reactive, aluminium does not corrode in air nor is it affected by water, even at high temperatures. The considerable resistance to corrosion arises from the fact that a thin film of aluminium oxide is formed over the surface of the metal. The oxide film serves as a protective coating and inhibits further attack.

1. Aluminium reacts with oxygen at high temperature and the reaction is strongly exothermic.

$$4Al + 3O_2 \longrightarrow 2Al_2O_3 + 798.18 \text{ kcal}$$

Because of the high heat of formation of Al_2O_3, aluminium powder can be used as a powerful reducing agent for many metal oxides. So much heat is released in these reactions that the temperature goes upto 3000°C and the reduced metal is obtained in the molten state. The reduction of metal oxides involving aluminium as a reducing agent is termed as thermite process. A particular thermite process involves conversion of Fe_2O_3 to molten iron.

$$Fe_2O_3 + 2Al \longrightarrow 2Fe + Al_2O_3$$

The process is often employed in welding and cutting operation.

2. Dilute and concentrated HCl dissolves Aluminium, liberating Hydrogen.

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$$

3. Dil. H_2SO_4 has no action on Aluminium, but hot conc. H_2SO_4 dissolves it yielding Sulphur dioxide.

$$2Al + 6H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3SO_2 + 6H_2O$$

4. Dil. HNO_3 slowly dissolves the metal liberating H_2. In conc. HNO_3 aluminium forms a protective oxide film on the metal surface and become passive.

$$2Al + 6HNO_3 \longrightarrow 2Al(NO_3)_3 + 3H_2$$

5. It readily dissolves in hot caustic soda forming Sodium aluminate.

$$2Al + 2NaOH \longrightarrow 2NaAlO_2 + 3H_2$$

6. Aluminium reacts with halogens to yield trihalides; with sulphur it yields a sulphide and with nitrogen it gives a nitride.

$$2Al + 3X_2 \longrightarrow 2AlX_3$$

$$2Al + 3S \longrightarrow Al_2S_3$$

$$2Al + N_2 \longrightarrow 2AlN$$

COMPOUNDS

1. **Oxides**:

Sequioxide, M_2O_3 can be made by heating the elements in oxygen, although B_2O_3 is usually made by dehydrating Boric Acid.

$$\underset{\text{Ortho Boric acid}}{H_3BO_3} \xrightarrow{100^\circ C} \underset{\text{Meta Boric acid}}{HBO_2} \xrightarrow{\text{red Heat}} B_2O_3$$

Being a non-metallic oxide, B_2O_3 is acidic in nature and is the anhydride of H_3BO_3. On heating with a metal oxide (as in Borax Bead Test), it gives metaborate, which has its own characteristic colour.

$$Co + B_2O_3 \longrightarrow \underset{\text{Blue}}{Co(BO_2)_2}$$

Al_2O_3 can be made by dehydrating $Al(OH)_3$ or from the elements. Al has a very strong affinity for O_2 and the heat of formation of Al_2O_3 is over 700 K Cal, hence it is used in the *thermite* reduction of the metal oxides.

$$4Al + 3O_2 \longrightarrow 2Al_2O_3 + 798 \text{ K Cal}$$

$$3Mn_3O_4 + 8Al \longrightarrow 4Al_2O_3 + 9Mn.$$

$Al(OH)_3$ is precipitated as a white gelatinous substance in qualitative analysis and is amphoteric. Generally it acts as a base giving salts with acids:

$$Al(OH)_3 \longrightarrow Al^{+3} + 3OH^-$$

It also acts as an acid to give aluminates.

$$Al(OH)_3 \longrightarrow H^+ + AlO_2^- + H_2O$$

$$Al(OH)_3 \longrightarrow 3H^+ + (AlO_3)^{-3}$$

$Al(OH)_3$ dissolves in NaOH forming sod. aluminate but is reprecipitated by the addition of CO_2 or trace of acid, since its acid properties are very weak.

$$\underset{}{Al(OH)_3} + \underset{\text{(Acid)}}{3H_3\overset{+}{O}} \longrightarrow [Al(H_2O)6]^{+3}$$

$$Al(OH)_3 + \underset{\text{(Alkali)}}{OH^-} \longrightarrow \underset{\text{(aluminate ion)}}{AlO_2^- + 2H_2O}$$

2. **Aluminium Sulphate & Alum:**

$Al_2(SO_4)_3$ may be formed by the action of H_2SO_4 on Bauxite

$$Al_2O_3xH_2O + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + (3 + X)H_2O$$

A solution containing equimolar proportion of $Al_2(SO_4)_3 + K_2SO_4$ on evaporation yields crystals of double salt along with $24H_2O$,

$$K_2SO_4 . Al_2(SO_4)_3 . 24H_2O, \text{ Common alum}$$

Alum is water soluble and on strong heating loses the water of crystallisation, changing into a porour mass. Both these salts are widely used in dyeing. From these salts $Al(OH)_3$ is deposited as a gelatinous precipitate on the cloth and has greater tendency for absorption of the dye and thus fixes it firmly to the cloth.

The process is called mordanting and the aluminium salt, the mordant.

Alum is also used for the purification of water, coagulation of colloidal substance, tanning of hides and sizing of paper.

3. **Borax :–**

($Na_2B_4O_7 . 10H_2O$) is the most important compound of Boron and is obtained by crystallising Kermite ($Na_2B_4O_7 . 4H_2O$) from water below 55°C. It may also be prepared from H_3BO_3 (Boric acid) by treatment with Na_2CO_3.

$$4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2$$

Molten Borax dissolves metal oxides, a property used in cleaning metal surface before soldering or welding. Certain metal oxides give characteristic colour to Borax when dissolved in it. The property may therefore be used as qualitative test for these metals. For example, Cr_2O_3 imparts a green colour to the borax bead. Borax is also used as water softener, soap filter, and an ingredient of glazes and pyrex glass.

QUESTIONS

1. What is the significant difference between Boron and the other members of the family?

2. Compare and contrast the chemical behaviour of (i) B & Al (ii) Boron and Li.

3. Explain the decrease of acidic character of the elements with rise in Atomic number.

4. Give the composition, properties and uses of (i) Borax (ii) Boron (iii) Alums.

5. Account for the change in Basic character of the Hydroxides in going down group IIIA.

6. Explain why (i) Aluminium does not corrode as easily as Iron ? (ii) $Al(OH)_3$ acts as an amphoteric compound?

7. Name the chief ores of aluminium, how is it extracted from them? Give some of its important reactions.

CHAPTER 6

GROUP IV A

Carbon, Silicon, Germanium, Tin and Lead

Carbon, Silicon, Germanium, Tin and Lead comprise the fourth group of representative elements. The physical data of the members of the group are listed in the table. All the members of the group possess the ability to utilize the valence electrons for the formation of four tetrahedral (Sp^3) covalent bonds, thereby attaining inert gas configuration. The great tendency of 4 covalency is the chief characteristic of the chemistry of carbon, which forms electron-pair bonds of great strength with hydrogen, halogen, nitrogen, oxygen, sulphur and with other carbon atoms. The chemistry of carbon differs significantly from that of the other members of the group. An outstanding property of carbon is its pronounced ability for self linkage (Catenation). This ability diminishes sharply for silicon, germanium, and tin, and is practically non-existent for lead. In comparision with the other members of its group, carbon is unique in its ability to form stable multiple bonds with other carbon atoms and also with other non-metallic atoms such as nitrogen, oxygen and sulphur. Thus, the following linkages are among those encountered:

$$>C=C<,\ -C\equiv C-, C\equiv N:,\ >C=\ddot{\underset{\cdot\cdot}{O}} \text{ and } >C=S$$

Of the members of this group carbon and silicion are non-metals. Germanium is a metalloid, while tin and lead are metals. Tin and lead besides forming 4 covalent bonds also exhibit oxidation state of + 2 in their ionic compounds *e. g.*, $SnCl_2$ and $PbCl_2$.

PHYSICAL DATA FOR GROUP IV ELEMENTS

Element	Symbol	At.No.	Electronic configuration	Atomic Radius °A	M.P. (°C)	B.P. (°C)
Carbon	C	6	[He] $2S^2 2p^2$	0.77	3500	4347
Silicon	Si	14	[Ne] $3S^2 3p^2$	1.17	1440	2600
Germanium	Ge	32	[Ar] $3d^{10} 4S^2 4p^2$	1.22	958	2700
Tin	Sn	50	[Kr] $4d^{10} 5S^2 5p^2$	1.41	232	2337
Lead	Pb	82	[Xe] $4f^{14} 5d^{10}$ $6S^2 .6p^2$	1.54	327	1750

Carbon:

The chemistry of the carbon compounds is, strictly speaking, organic chemistry. In this chapter we will limit our study of carbon to the element and its inorganic compounds.

International Union of Pure and Applied Chemistry (I.U.P.A.C.) in 1959 recommended that from 1961 carbon should be adopted as the primary standard for atomic weights in place of oxygen, the atomic weight of carbon being fixed as exactly 12. The atomic weight of oxygen will become slightly less than 16, and all other atomic weights will have to be slightly adjusted. Oxygen has been the standard element ever since Berzelius adopted it in his work on equivalents (1819).

Carbon exists in two allotropic forms, diamond and graphite. The various types of 'Amorphous' Carbon, such as charcoal lamp-black, anthracite are now known to have an imperfect graphite structure. Allotropy is the existence of an element in two or more forms, in the same physical state. Allotropy is due to the existence of different arrangements of atoms or molecules in a crystal e.g., Carbon, Sulphur and Phosphorus or it may result from the existence of two or more kinds of molecules, e.g., Oxygen (O_2) and Ozone (O_3).

Graphite. In an impure state, graphite is found in nature in several parts of the world. Pure artificial graphite is made by mixing powdered charcoal, coke or anthracite with sand and heating the mixture in an electric furnace. Air is excluded by covering the mixture with more sand. Silicon carbide (Carborundum) is probably formed first, and then this compound dissociates into carbon and silicon

$$SiO_2 + 3C = SiC + 2CO$$

$$SiC = Si + C$$

The important properties of graphite are that in contrast to diamond, it is soft, and non-metallic substance that conducts electricity quite well. It is soft because the atom of its giant molecules are linked in a mass of condensed benzene rings, lying in one plane, and each carbon atom forming a unit of three adjacent rings. The planes are held together only by weak Vander Waals

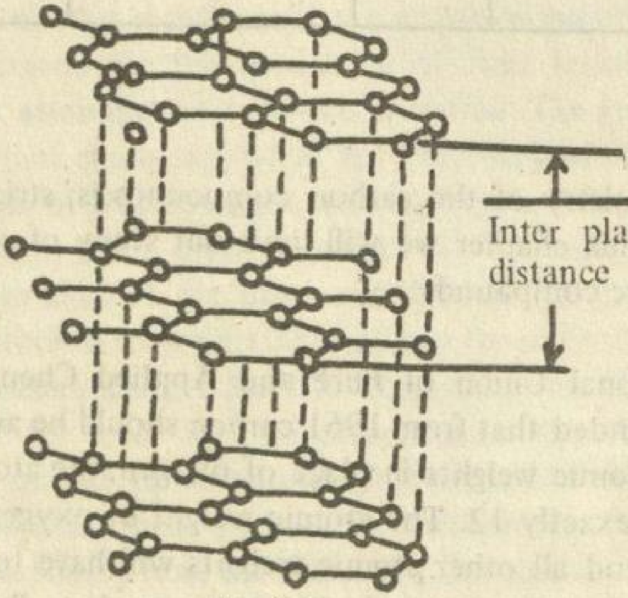


Fig. 6.1

forces and under stress one layer can slide easily over the next. This is the secret of its flaky nature and its excellent properties as a lubricant. Graphite electrodes may be used where metals are out of question as for example, anodes where chlorine is evolved. Graphite is used also as the familiar 'black-lead' for making pencils, and for the preparation of refractory crucibles. It is also used as a moderator in Nuclear Reactors.

Diamond. Natural diamonds are found chiefly in South Africa. They usually occur in what is known as 'blue ground' which is mainly magnesium orthosilicate, Mg_2SiO_4. Some small black diamonds are also found in association with graphite, Diamond is one of the hardest substance known, its hardness being due to its crystal structure. In this structure the gaint molecule is built of mass of carbon atoms symmetrically arranged, each carbon atom being joined to four others by very strong covalent bonds directed to the apices of a regular tetrahedron.

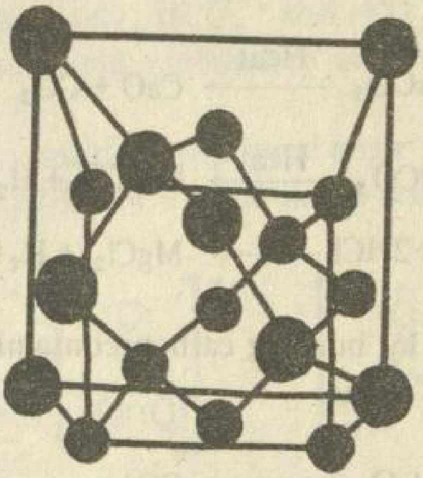


Fig. 6.2

Natural diamond has no attractive appearance until it has been cut to a certain Pattern. Diamond has a very high refractive index and if stone be cut to correct shape nearly all the light that falls on it may be emitted again by total internal reflection. This explains why the gem-stone is so brilliant and also why the 'back' of the cut stone appears dark. The uses of diamond are chiefly concerned with jewellery, with tipping, drilling and cutting tools and with wire-drawing.

Diamond is chemically inert and does not burn in air until a temperature of 900°C is reached. Unlike graphite, acids do not affect it but it is slowly oxidized when heated with a potassium dichromate/sulphuric acid mixture.

Oxides of Carbon:

Carbon Dioxide CO_2: Carbon dioxide gas can be obtained by the action of heat on metallic carbonates or bicarbonates, or by the action of dilute mineral acids, such as hydrochloric or nitric, on the same compounds.

$$CaCO_3 \xrightarrow{\text{Heat}} CaO + CO_2$$

$$2NaHCO_3 \xrightarrow{\text{Heat}} Na_2CO_3 + H_2O + CO_2$$

$$MgCO_3 + 2HCl \longrightarrow MgCl_2 + H_2O + CO_2$$

It is also formed by burning carbon containing materials (wood, coal, charcoal, etc.) in excess of air.

$$C + O_2 \longrightarrow CO_2$$

It is also the by-product of the fermentation of molasses

$$C_6H_{12}O_6(aq) \xrightarrow[\text{(Enzyme)}]{\text{Zymase}} \underset{\text{Alcohol}}{2C_2H_5OH} + 2CO_2 \uparrow$$

CO_2 is used in refrigeration, in the preparation of bottled beverages, for fire extinguishing, for the storage of fruit, and for the manufacture of carbonate, such as H_2CO_3. It is weak acid which changes the colour of litmus solution to a winered colour, but does not affect methyl orange. It ionizes to hydrogen and bicarbonate ions.

$$H_2CO_3 \longrightarrow H^+ + HCO_3^-$$

and according to conditions, the bicarbonate ions may either hydrolyse giving hydroxyl ions in solution, or break down further into carbonate and hydrogen ions.

$$\text{(Hydrolysis) } HCO_3^- + H_2O \longrightarrow H_2CO_3 + OH^-$$

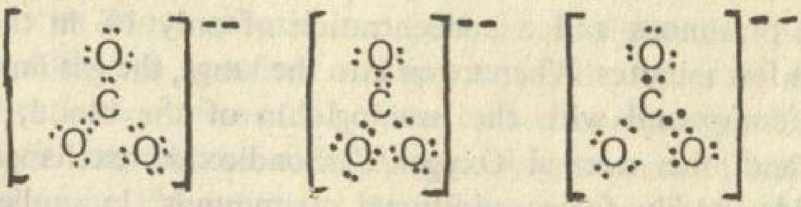
$$\text{(Further ionization) } HCO_3^- \longrightarrow CO_3^{-2} + H^+$$

The molecule of carbon dioxide is linear, and there is no one formula that truly represents it. It is a resonance hybrid to which the following structures contribute significantly:

(a) $\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}: :C: :\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}$ (b) $:\overset{+}{\underset{\cdot\cdot}{O}}: : :C:\overset{-}{\ddot{O}}:$ (c) $:\overset{-}{\underset{\cdot\cdot}{\ddot{O}}}:C: : :\overset{+}{\underset{\cdot\cdot}{O}}$

Two types of salts, the hydrogen carbonates (bicarbonates) and the normal carbonates containing, respectively, HCO_3^- and CO_3^{-2}, are derivable from carbonic acid. Bicarbonates yield carbonates on thermal decomposition.

The carbonate ion is coplanar, with bond angle of 120° and a C–O distance of 1.31 A°. The properties of the ion are in accord with the resonance formulations shown:



Carbon Monoxide, CO :

Carbon monoxide is fromed almost quantitatively by the combustion of carbon in an insufficient supply of air at 1000°; at temperatures in the neighbourhood of 500° carbon dioxide is practically the sole product, even when carbon is present in excess. Commercially, carbon monoxide alongwith H_2 is obtained largely by the oxidation of hot coke by steam. The mixture is known as *water gas* and used as a fuel.

$$H_2O\,(g) + C \longrightarrow \underset{\text{water gas}}{\underline{H_2 + CO}}$$

CO may be separated by liquefaction and cooling which does not affect hydrogen gas. The pure gas is best obtained by dehydrating pure formic acid with conc. sulphuric acid washing it free from traces of sulphur dioxide, and drying. Oxalic acid may also be used in place of formic but this method necessitates the removal of CO_2 also:

$$\text{(With Formic Acid) } HCOOH \xrightarrow{-H_2O} CO + H_2O$$

$$\text{(With Oxalic Acid) } (COOH)_2 \xrightarrow{-H_2O} CO + CO_2 + H_2O$$

The action of conc. sulphuric acid warmed with potassium ferrocyanide gives a fairly pure gas. (dil. acid gives the extremely poisonous hydrogen cyanide)

$$K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O \longrightarrow 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4 + 6CO$$

Carbon monoxide is a colourless gas that burns with the blue flame. It is extremely poisonous and a concentration of only 1% in the air can cause death in a few minutes. When taken into the lungs, the gas immediately form a scarlet compound with the haemoglobin of the blood, 'Carboxy haemoglobin,' and the normal Oxygen/Carbondioxide exchange ceases. Carbon monoxide readily forms additional compounds. In sunlight, or in the presence of active charcoal, it combines directly with chlorine to give another very poisonous gas, carbonyl chloride or phosgene

$$CO + Cl_2 \longrightarrow COCl_2$$

Carbon monoxide also forms gaseous carbonyls with some metals; iron, cobalt, nickel, a number of other transition metals. Compound formed with nickel $Ni(CO)_4$ is of industrial importance

$$Ni + 4CO \xrightarrow{60^\circ C} Ni(CO)_4$$

Carbon monoxide is believed to be a resonance hybrid between three structures:

$$\text{(a) } :\overset{-}{C}:::\overset{+}{O}: \quad \text{(b) } :C::\underset{\cdot\cdot}{\ddot{O}} \quad \text{(c) } .:\overset{+}{C}\ :\underset{\cdot\cdot}{\overset{-}{\ddot{O}}}:$$

Carbides: Carbon combines **with metals** and non-metals to form carbides. Calcium carbide, CaC_2, is obtained by heating CaO and C in an electric furnace.

$$CaO + 3C \longrightarrow CaC_2 + CO$$

Calcium carbides reacts with water to form acetylene

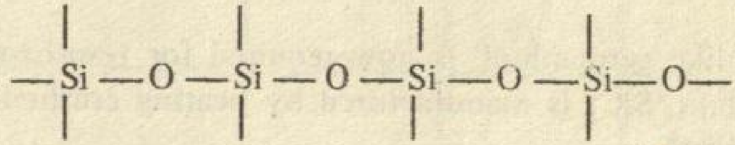
$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

It also reacts with nitrogen to give calcium cynamide:

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

SILICON

Silicon shows physical and chemical relationship both to boron and carbon. Although growing in importance, the range of silicon compounds is not nearly as wide as that of the carbon compounds. One reason for this is that although silicon clearly shows the property of self-linkage, yet after seven or eight silicon atoms have joined in a chain by covalent bonding, the molecule becomes unstable and breaks up. Silicon is not found free in nature: but in chemical combination as silica, silicates etc. It is more abundant in the earth's crust than any other element except oxygen. In natural complex silicate minerals, silicon atoms often alternate in chains or rings with those of oxygen thus:



$$-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-O-$$

and this seems to afford a much more stable arrangement than the chain of silicon atoms only.

The element silicon can be obtained by the reduction of the oxide, silica, of SiO_2. Magnesium will react with silica at fairly low temperature, but there is always a certain amount of magnesium silicide formed with the silicon:

$$SiO_2 + 2Mg \longrightarrow 2MgO + Si$$

Excess of megnesium is necessary to ensure that all the silica is decomposed, otherwise the silicon and silica would be difficult to separate. The formation of the silicide to some extent cannot, therefore, be avoided:

$$Si + 2Mg \longrightarrow Mg_2Si$$

Crystalline silicon does not burn at all readily, but the amorphous form does ignite in oxygen at a temperature of 400°C. Common mineral acids have no effect on silicon, but a mixture of concentrated nitric and hydrofluoric acid convert it to the tetrafluoride, SiF_4. Fairly concentrated caustic alkali solutions dissolve it readily, forming a silicate and hydrogen:

$$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2$$

It will, like carbon, decompose steam at a red-heat but much more slowly.

$$Si + 2H_2O \longrightarrow SiO_2 + 2H_2$$

Silicon nitride, Si_3N_4, is a refractory material that is very resistant to thermal shock.

The element dissolves in many molten metals forming Silicides, some of which have commerical importance. Most of the silicides are hard crystalline substances with a metallic lustre. Ferro silicon, FeSi, is used in the manufacture of special silicon steels.

Pure silicon, like germanium, is now required for transistors. Silicon carbide (Carborundum, SiC) is manufactured by heating crushed coke and sand in an electric furnace:

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

It is almost as hard as diamond; crystal structure does not greatly differ from that of the diamond. It is used as an abrasive, and as refractory furnace lining.

Silicon Dioxide: SiO_2 (Silica):

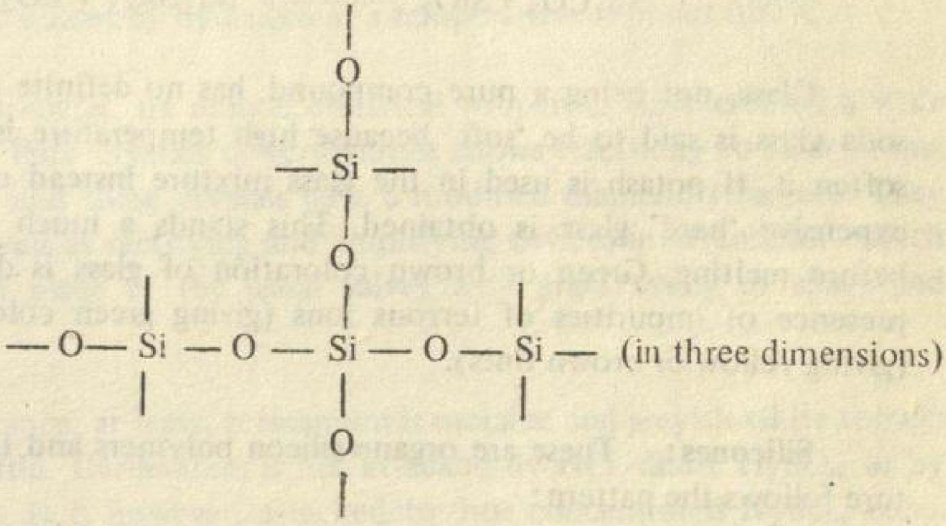
Apart from the natural occurrence of silica in combination with other oxides as silicates, the dioxide itself exists in several forms. These include quartz, tridymite, cristobalite, and Kieselguhr. Quartz is the stable form of silica and varieties of this include; sand, rock-crystal, and some gem-stones.

In laboratory pure silica can be obtained by the hydrolysis of silicon tetrafluoride or by dehydrating silicic acid which itself is prepared by the action of hydrochloric acid on sodium silicate solution:

$$Na_2SiO_3 + 2HCl \longrightarrow H_2SiO_3 + 2NaCl$$

$$H_2SiO_3 \longrightarrow SiO_2 + H_2O$$

The structure of silicon dioxide is nothing like that of carbon dioxide which exists as simple molecules. All forms of silica consists of three dimensional net works of linked silicon and oxygen atoms. In this network every oxygen atom is common to two tetrahedral SiO_4 groups. The three forms of silica differ in the mode of stacking of the relatively large oxygen atoms.



Silica dissolves readily in hot concentrated caustic alkali solution forming silicates:

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

SILICATES AND GLASS

Sodium Silicate Na_2SiO_3:

This forms as a glass, when sodium carbonate is heated with silica at a high temperature:

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$

Sodium silicate is used in detergent mixtures (to keep loosened dirt in suspension and to lessen any attack on aluminium), and on account of its adhesive properties, for the large scale manufacture of card-board packaging.

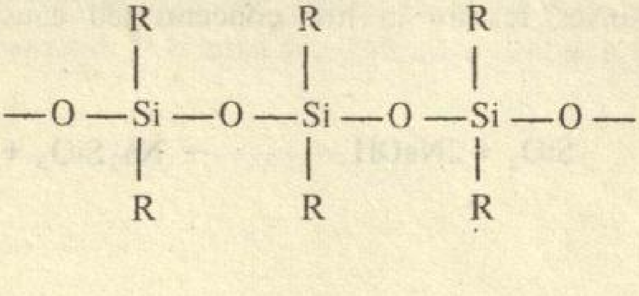
Glass. Cheap glass is made by fusing together sand, limestone, and alkali. If soda is used as the alkali the glass produced is essentially a mixture of sodium and calcium silicates.

$$CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2$$

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$

Glass, not being a pure compound, has no definite melting point and soda glass is said to be 'soft' because high temperature is not necessary to soften it. If potash is used in the glass mixture instead of soda, the more expensive 'hard' glass is obtained. This stands a much high temperature before melting. Green or brown coloration of glass is due mainly to the presence of impurities of ferrous ions (giving green colour) or ferric ion (giving yellow or brown tints).

Silicones: These are organo-silicon polymers and their general structure follows the pattern:



$$-\mathrm{O}-\underset{\textstyle\mathrm{R}}{\underset{|}{\overset{\textstyle\mathrm{R}}{\overset{|}{\mathrm{Si}}}}}-\mathrm{O}-\underset{\textstyle\mathrm{R}}{\underset{|}{\overset{\textstyle\mathrm{R}}{\overset{|}{\mathrm{Si}}}}}-\mathrm{O}-\underset{\textstyle\mathrm{R}}{\underset{|}{\overset{\textstyle\mathrm{R}}{\overset{|}{\mathrm{Si}}}}}-\mathrm{O}-$$

R represents an organic radical, and these repeating units may be in straight chains or rings.

A modern method of preparing silicones is as follows:

Methyl chloride vapour is passed at 300°C over powdered silicon containing a little copper as catalyst. The product consists mainly of three substituted silanes. Trimethyl chlorosilane $(CH_3)_3ClSi$, dimethyl dichlorosilane $(CH_3)_2Cl_2Si$, and monomethyl trichlorosilane, CH_3Cl_3Si. These are separated by the process of fractional distilation. They are then hydrolysed to give various silicones.

The Silicones are used as water repellent and are excellent for water proofing fabrics. They are also used as lubricants and insulating and polishing materials.

Germanium: The probable existence of germanium was predicted as 'eka-silicon' by Mendeleef in 1871. It was actually discovered in 1886. It is fairly widespread, but usually only in very small quantities. It is associated with the sulphide ores of metals such as copper, silver, lead and zinc. The isolation of the metal is not easy, but perhaps the best method is the reduction of the oxides by hydrogen at a temperature of about 600°C.

As a semi-metal, its unique electrical properties have created a wide demand for it. Pure crystals of germanium allows electricity to flow in one direction only, and these crystals have a modified diamond structure. They are now employed as rectifying and amplifying devices in 'Transistor' which can be used in place of the usual valves with great saving of space and electricity.

In appearance, at least, germanium is metallic and greyish-white though it is rather brittle. Germanium is not attacked by HCl, dilute H_2SO_4 or by alkali solutions. It is however, attacked by hot concentrated H_2SO_4 conc. HNO_3 or fused caustic alkali. Concentrated nitric acid converts it directly to germanium oxide, GeO_2. Only three hydrides have been prepared, GeH_4, Ge_2H_6, and Ge_3H_8, and these are less stable than the silanes.

Tin:

Tin is sometimes found native. Its chief ore is cassiterite or tinstone, SnO_2.

Tinstone contains about 10% of tin as SnO_2 and the rest is all impurity. The chief impurity is silicious matter, other substances present being tungstates of iron and manganese and pyrites of iron, copper and arsenic. The extraction involves the following steps :-

(i) Concentration.

(ii) Roasting and Reduction.

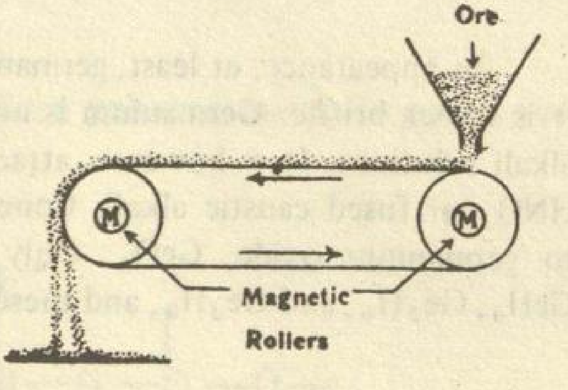
(iii) Refining.

(i) Concentration. The well-powdered ore is concentrated by gravity. On washing in a stream of water, the lighter silicious particles are carried away while the heavier ore particles settle to the bottom.

(ii) (a) Roasting. On heating the concentrated ore in the presence of excess of air, the arsenic and sulphur are removed as As_2O_3 and SO_2 respectively while the iron and copper pyrites are converted to oxides and sulphates.

(b) Electromagnetic separation. The tungstates of Iron and Manganese are magnetic in nature and are removed from SnO_2, by dropping the roasted mass on a moving belt over magnetic rollers. Tinstone being non-magnetic, falls off undeflected, whereas the magnetic wolfram and Iron oxide, a separate heap near the magnet.

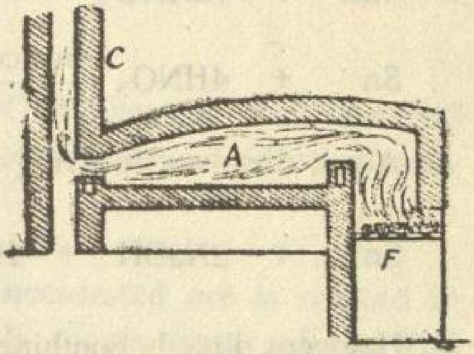
The mass is finally washed to remove Copper and Iron Sulphates. The Tin concentrate thus obtained, is subjected to smelting.



(c) Smelting or Reduction.

It is now mixed with anthracite (carbon) and a little limestone ($CaCO_3$) and heated in a small reverberatory furnace. The oxide is reduced to the metal while some of the impurities, if still present, are slagged off.

$$SnO_2 + 2C \text{ -------- } Sn + 2CO$$



Molten tin collects at the base of the hearth and is drawn off and cast into blocks known as block tin.

(iii) Refining.

The refining of the crude tin is done by liquation process. The tin blocks are remelted and allowed to flow away from the higher melting impurities. This may further be purified by electrolysis. As usual the impure tin is made the anode while pure tin as cathode and the bath consists of H_2SiF_6 and H_2SO_4.

Properties.

Tin occurs in three alotropic forms:–

(i) Grey Tin ------ stable below 18°C.

(ii) White Tin ------ stable above 18°C to 170°C

(iii) Rhombic Tin ------ stable above 170°C.

$$\text{Grey Tin} \xrightarrow{18^\circ C} \text{White Tin} \xrightarrow{170^\circ C} \text{Rhombic Tin.}$$

Tin is not affected by air at ordinary temperature, but burns to tin oxide, SnO_2. at about 1500°C. Tin dissolves in HCl giving $SnCl_2$ and evolving H_2. Conc H_2SO_4 gives $Sn(SO_4)_2$ but dil H_2SO_4 gives $SnSO_4$.

$$Sn + H_2SO_4 \text{ (dil)} \longrightarrow SnSO_4 + H_2$$

$$Sn + 4H_2SO_4 \text{ (Conc)} \longrightarrow Sn(SO_4)_2 + 2SO_2 + 4H_2O$$

It is also dissolved in dil. HNO_3 forming $Sn(NO_3)_2$ and NH_4NO_3. whereas Sn is converted to H_2SnO_3 in hot conc. HNO_3 :

$$4Sn + 10HNO_3 \xrightarrow{(dil)} Sn(NO_3)_2 + H_2$$

$$Sn + 4HNO_3 \xrightarrow{hot\ conc} H_2SnO_3 + 4NO_2 + H_2O$$

Alkali dissolves tin giving alkali metal stannate:

$$Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + 2H_2$$

Halogens directly combine with Sn to give SnX_4. Thus,

$$Sn + 2Cl_2 \longrightarrow SnCl_4$$

Tin forms stannous as well as stannic compounds. An aqueous solution of stannous chloride is a powerful reducing agent and it reduces Ferric to Ferrous, Mercuric to Mercurous, and Cupric to cuprous ions.

$$2Fe^{+3} + Sn^{+2} \longrightarrow 2Fe^{+2} + Sn^{+4}$$

Stannic chloride is a covalent compound and is rapidly hydrolysed by excess water, especially if heated, to form 'stannic hydroxide', hydrated tin oxide.

$$SnCl_4 + 4H_2O \longrightarrow SnO_2 . 2H_2O + 4HCl$$

Uses.

(i) In tin-plating ——— Iron sheets coated with tin either mechanically or electrolytically are used for making Vegetable ghee tins.

(ii) Tinning——— Household utensils are protected from corrosion and the effect of organic acids in food-stuffs by tinning.

(iii) Tin foil is used for wrapping cigarettes, confectionery etc.

(iv) Its alloys find various applications in arts and industries.

Lead

Lead occurs mainly as galena (lead sulphide) and this ore is usually found with Zinc blende (Zinc sulphide).

Metallurgy: PbS is easily converted to PbO by heating in air and PbO is then easily changed to Pb by reduction with carbon or scrap iron or simply by air,

(1) **Air Reduction Process**: The concentrated ore is roasted in reverberatory furnace under controlled supply of air. Some of the PbS is converted to $PbSO_4$ and PbO which now react with the excess of PbS and thereby reduced to metallic Pb. The molten lead is drawn off and further purified:

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$

$$PbS + 2O_2 \longrightarrow PbSO_4$$

$$2PbO + PbS \longrightarrow 3Pb + SO_2$$

$$PbSO_4 + PbS \longrightarrow 2Pb + 2SO_2$$

(2) **Carbon Reduction Process**: The crushed and concentrated galena is converted to PbO by roasting with a slow blast of air.

$$PbS + O_2 \longrightarrow PbO + SO_2$$

The Oxide ore is then charged in blast furnace with coke and lime. PbO is thus converted to Pb. The molten lead sinks at the bottom of the furnace and the slag floats on the top of the molten lead and is drawn off from different outlets.

$$PbO + C \longrightarrow Pb + CO$$

$$PbO + CO \longrightarrow Pb + CO_2$$

Properties:

Lead is melleable, soft, bluish grey metal. By slow heating with air, Pb is converted to PbO, and at high temperature it is converted to red lead Pb_3O_4.

$$2Pb + O_2 \longrightarrow 2PbO$$

$$6PbO + O_2 \xrightarrow{\text{red heat}} 2Pb_3O_4$$

Lead does not react with dil. HCl or H_2SO_4 but with conc. HCl it gives hydrogen, and with conc. H_2SO_4, SO_2.

$$Pb + 2HCl \longrightarrow PbCl_2 + H_2$$

$$Pb + 2H_2SO_4 \longrightarrow PbSO_4 + 2H_2O + SO_2$$

It is attacked by sulphur, fluorine and chlorine:

$$Pb + S \longrightarrow PbS$$

$$Pb + 2Cl_2 \longrightarrow PbCl_4$$

Uses:

Some of the uses of lead are:

(1) Manufacture for lead accumulators.

(2) Covering for electric cables.

(3) Lead chambers in H_2SO_4 plants.

(4) Manufacture of lead tetraethyl.

(5) Manufacture of white lead and other pigments.

(6) Making alloys, such as solder, type metal, etc.

Lead tetraethyl:

An important compound of lead is tetraethyl lead (TEL), $Pb(C_2H_5)_4$ it is used as anti-knock in internal combustion engines using petrol, (i.e. prevent premature explosive combustion). Lead tetraethyl is now being

8. Write equations for the following reactions.

(a) Lime water + $CO_2 \longrightarrow$

(b) CaC_2 + water $\longrightarrow$

(c) SiO_2 + heat $\longrightarrow$

(d) $Si + NaOH + H_2O \longrightarrow$

(e) $CO + Ni \xrightarrow{60^\circ C}$

(f) Potassium ferrocyanide + Conc. $H_2SO_4 \longrightarrow$

(g) $HCOOH$ + Conc. $H_2SO_4 \longrightarrow$

(h) $Si + Mg \xrightarrow{heat}$

(i) $Fe^{+3} + Sn^{+2} \longrightarrow$

(j) $SnCl_4 + H_2O \longrightarrow$

(k) $PbS + O_2 \longrightarrow$

(l) $PbO + C \longrightarrow$

(m) $CO + Cl_2$

CHAPTER 7

GROUP V A NITROGEN FAMILY

Group V A consists of Nitrogen, Phosphorus, Arsenic, Antimony and Bismuth.

The electronic configuration and Oxidation states of these elements are given in Table 7.1.

Table 7.1

Element	At.No.	Electronic configuration	Oxidation States.
Nitrogen	7	[He] $2S^2\ 2p^3$	$-1, \pm 2, +3, +4, +5$
Phosphorus	15	[Ne] $3S^2\ 3p^3$	$\pm 3, +5$
Arsenic	33	[Ar] $3d^{10}\ 4S^2\ 4p^3$	$\pm 3, +5$
Antimony	51	[Kr] $4d^{10}\ 5S^2\ 5p^3$	$\pm 3, +5$
Bismuth	83	[Xe] $4f^{14}\ 5d^{10}\ 6S^2\ 6p^3$	$\pm 3, +5$

The valence shell of the members of this group have a general configuration of $ns^2 np^3$.

The members of nitrogen family have 5 electrons in the valence shell and need three electrons to complete their 'Octet', which they do so by sharing of electrons with other atoms. Oxidation state of –3,+3 and +5 are common for all the elements of this group. They show a maximum of oxidation state of +5 by using all the five electrons in the valence shell in forming bonds. The tendency of the shared Pair of S electrons to remain inert (the inert Pair effect,) increases with the increase in atomic weight. Thus only the p electrons are used in bonding showing +3 oxidation state of the element. In the case of nitrogen, oxidation states –2, +1, +2, and +4 are also important. Some of the physical properties are given in table 7.2.

Table 7.2

Symbol	At. Wt	Atomic radius A°	M.P °C	B.P °C	First I.P (e v)	E.N.
N	14.01	0.74	–210	–196	14.5	3.1
P	30.98	1.10	444.1	2800	11.0	2.1
As	74.91	1.21	814 (36atm)	615 (Sub-lime)	10.0	2.1
Sb	121.76	1.41	631	1380	8.6	1.8
Bi	209.00	1.52	271	1560	8.0	1.7

Table 7.2 shows that there is an increase in electropositive (metallic) character down the group. Nitrogen and Phosphorus are non-metals. arsenic and antimony are semi-metals (metalloids) and bismuth a typical metal. Thus, the oxides of nitrogen and phosphorus are strongly acidic. whereas those of arsenic and antimony are amphoteric and that of bismuth largly basic. The increasing basicity of oxide, going down the group is mainly attributed to the increasing size of the elements.

High ionization potential value of nitrogen as compared to bismuth indicate that it is more difficult to remove electrons from nitrogen atom than from bismuth atom. Since nitrogen atom is a small one, it holds its electrons more firmly and forms multiple bonds. Under ordinary conditions , other members of the group are not able to form multiple bonds so they do not exist in diatomic state. Instead, at least in some of their allotropic forms phosphorus, arsenic and antimony occur as separate tetratomic, tetrahedral molecules. The tendency to form covalent linkages is reduced as we move down the group.

Tendency to form ionic compound in this group is less common as compared with the elements of group I, II, VI & VII, this is beacuse of intermediate electronegativity values. A wide range of behaviour in group V; shown by anion formation by nitrogen and cation formation by bismuth e.g., Li_3N and BiF_3. Nitrogen is the only member of the group which can accept three electrons to complete its octet, thus forming N^{-3} , the nitride ion. However, the loss of all five valence electrons is not encountered because no M^{+5} cations are formed.

Anomalous Behaviour of Nitrogen:

As in all the groups of the periodic table, nitrogen, the first member of the V group, differs in many properties from the other elements of the group. The difference is due to (1) its small size, (2) a single screening K shell and (3) absence of "d" orbitals.

Due to its small size it has high electronegativity. This is the only element of this family which can form anion, N^{---} by accepting electrons, and form multiple bonds. It forms diatomic molecules which are very stable (Dissociation energy = 225 K. cals. per mole). There is a triple bond between the nitrogen in the molecule N : : : N.

As nitrogen has no "d" orbitals, it can have only a maximum of eight electrons in its valence shell. It cannot 'expand' its valence shell like other members of its family. For this reason nitrogen cannot act as the central atom in complex compounds as it cannot accept pairs of electrons from ligands. Other members can accept upto six pairs of electrons.

Occurrence:

Nitrogen is the only member of group V that occurs as a gas in the elemental state. It comprises about 78% (by volume) of the air. In combined form it occurs mainly as sodium nitrate (Chile salt peter). Plants and animals contain combined nitrogen in the form of proteins.

Phosphorus, because of its reactive nature it does not occur in free state. It occurs mostly in the form of phosphates, the simple Calcium phosphate $Ca_3(PO_4)_2$, and a mixed phosphate $CaF_2 . 3Ca_3(PO_4)_2$, known as apatite. Ores containing large percentages of phosphorus are commonly known as phosphate rocks. Phosphorus is an essential constituent of all living matter. Bones, for example, contain above 60% $Ca_3(PO_4)_2$. The human body contain 9% phosphorus.

Arsenic occurs principally as sulphide – orpiment (As_2S_3) realgar (As_4S_4) and arsenopyrite (FeAsS). It is also found in the free state in small quantities.

Antimony occurs chiefly in the mineral stibnite (Sb_2S_3). Small quantities of the element are also found in the free state. Bismuth is found in both the free and the combined state. The principal minerals of bismuth are bismuth galance (Bi_2S_3) and bismuth ocher (Bi_2O_3).

Preparation:

Nitrogen is obtained commercially by fractional distillation of liquid air. The liquid oxygen (b. p. – 183°C). The nitrogen being more volatile tends to boil off first in evaporation in fractionating column.

Pure nitrogen can be prepared in the laboratory by heating ammonium nitrite.

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

In practice, a mixture of $NaNO_2$ with NH_4Cl is heated as NH_4NO_2 is explosive.

$$NH_4Cl + NaNO_2 \longrightarrow NaCl + 2H_2O + N_2$$

It may also be prepared by heating ammonium dichromate.

$$(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + 4H_2O + N_2$$

Phosphorus is prepared industrially by heating a mixture of Phosphate rock, sand and coke to a high temperature in an electric furnace. The following reactions take place:

$$2Ca_3(PO_4)_2 + 6SiO_2 \longrightarrow P_4O_{10} + 6CaSiO_3$$

$$P_4O_{10} + 10C \longrightarrow P_4 + 10\,CO$$

The Phosphorus and carbon monoxide escape as vapours and the former is condensed under water as a white waxy solid.

Arsenic is easily obtained by reducing arsenious oxide, As_4O_6, with carbon.

$$As_4O_6 + 6C \longrightarrow 4As + 6CO$$

The element can also be obtained by heating the mineral arsenopyrite in the absence of air:

$$FeAsS \longrightarrow FeS + As$$

Antimony is prepared from the sulphide ore by roasting. The sulphide is converted to the oxide which may then be reduced by carbon in the form of Charcoal or Coke.

$$2Sb_2S_3 + 9O_2 \longrightarrow 2Sb_2O_3 + 6SO_2$$

$$Sb_2O_3 + 3C \longrightarrow 2Sb + 3CO$$

The metal can also be obtained from the sulphide ore by heating with scrap iron.

$$Sb_2S_3 + 3Fe \longrightarrow 2Sb + 3FeS$$

Bismuth is produced mostly as a by-product in the extraction of lead and in the refining of copper. Like arsenic and antimony it may be recovered from the sulphide ore by roasting, followed by reduction with carbon.

$$2Bi_2S_3 + 9O_2 \longrightarrow 2Bi_2O_3 + 6SO_2$$

$$Bi_2O_3 + 3C \longrightarrow 2Bi + 3CO$$

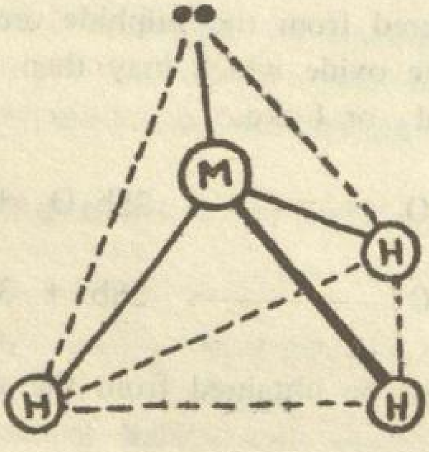
Compounds.

Hydrides:

All the elements of the nitrogen family form simple hydrides of formula MH_3. All are colourless gases under ordinary conditions.

Structure of hydrides:

The structure of these hydrides is Pyramidal or tetrahedral with one position occupied by a lone pair of electrons. (Fig 7.1). M is at the apex while the hydrogens are at the base making a triangle. Four equivalent hybrid orbitals are formed by mixing up the S and P orbitals of the valence shell. As there are five electrons in the valence shell, one of the four hybrid orbitals has a pair of electrons while the other three are half-filled with one electron each. Sigma overlap with hydrogens produce three sigma bonds.



Pyramidal structure of V group hydrides.
Fig. 7.1

Physical Properties:

Some of the important physical properties of the hydrides are given in Table 7.3.

Table 7.3

Name	Formula	M.P. °C	B.P. °C	Bond Angle	Bond Energy (K. cal)	Odour
Ammonia	NH_3	–77	–33	107	93	Pungent
Phosphine	PH_3	–133	–87.8	93°	76	fishy
Arsine	AsH_3	–113	–55	92°	59	garlic
Stibine	SbH_3	–88	–17	91	61	unpleasant.
Bismuthine	BiH_3	–	+ 22	90°	–	—

Stability:

Notice the bond energies of the hydrides decreases down the group. Hence the stability of the hydrides also decreases in the same order.

Hydrogen bonding:

The melting and boiling point of ammonia should be the lowest of all the hydrides as it is the lightest molecule. Actually these are almsot the highest. This is explained on the basis of great electronegativity of nitrogen. The bond between hydrogen and nitrogen is highly polarized. The nitrogen and hydrogen of different ammonia molecules which lie near attract each other. A weak link between nitrogen and hydrogens of adjacent molecules is formed. This is called 'Hydrogen Bond'. A very large number of ammonia molecules may be linked together in this manner. When ammonia is heated some of the heat is used in breaking the HYDROGEN BONDS. The M.P. and B.P. of ammonia are therefore unusually high.

Chemical Properties:

(1) Basic nature.

This is due to the presence of the lone pair of electrons on the atoms of the elements of group VA in their hydrides. Ammonia is strongly bacic and forms salts with all the acids. Since the shared electrons are nearer nitrogen, it can easily donate the lone pair of its electrons.

$$H_3\ddot{N} + H^+ \longrightarrow \overset{+}{N}H_4\text{(ammonium salt)} \quad (\text{E.Neg H} = 2.1)$$

$$(\text{E.Neg N} = 3.0)$$

The electronegativity of phosphorus and hydrogen are almost equal. Therefore the phosphorus in phosphine cannot donate its lone pair as easily as nitrogen in ammonia. The basic property is therefore much less developed. In fact phosphine shows its only basic reaction when it combines with hydrogen halides to form phosphonium salts.

$$H_3P: + HX \longrightarrow \overset{+}{P}H_4 + \bar{X}$$

The other hydrides do not show any basic reaction. Basic nature, therefore decreases down the group.

(2) Combustibility.

All the hydrides are combustible in air. Ammonia burns is air to form nitrogen and water. In presence of platinum, however ammonia gives nitric oxide.

$$4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O$$

Phophine is spontaneously combustible in air. The hydrides burns to produce oxyacids or oxides of the elements.

$$4PH_3 + 8O_2 \longrightarrow P_4O_{10} + 6H_2O \longrightarrow 4HPO_3$$

$$2SbH + 4O_2 \longrightarrow Sb_2O_5 + 3H_2O$$

(3) Reducing action.

All the hydrides are reducing agents. The reducing property increases, as the stability decreases, down the group.

$$2NH_3 + 3CuO \longrightarrow 3Cu + N_2 + 3H_2O$$

Preparation :

The most important industrial method for the production of ammonia is the Haber Process, in which nitrogen combines directly with hydrogen according to the equation:

$$N_2 + 3H_2 \longrightarrow 2NH_3 \quad \Delta H = -22.0 \text{ K Cal.}$$

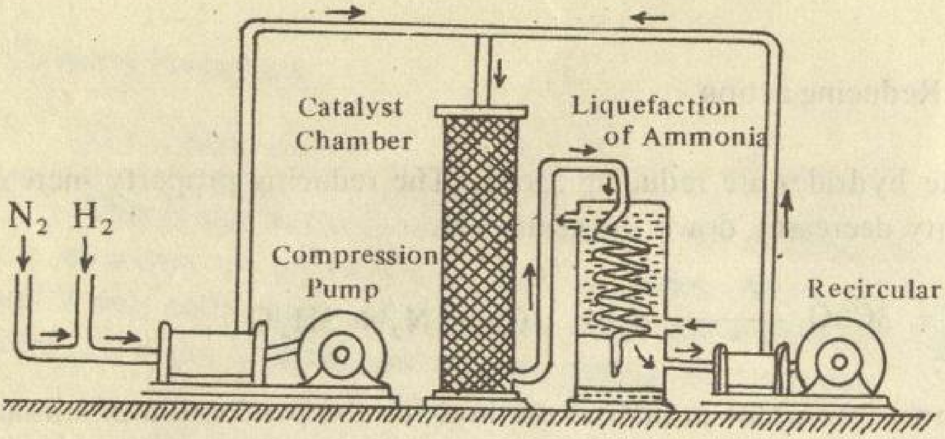
The above reaction is reversible and exothermic and is accompanied by a decrease in volume. Hence, according to Le-Chatelier' principle the maximum yield of ammonia can be had if

(i) The pressure be kept as high as practicable, the most suitable Pressure is found to be 200 atmospheres.

(ii) The temperature must be kept as low as Possible, a temperature of 500°C is found very suitable.

(iii) A catalyst may be used; the most efficient catalyst has been a mixture of Fe_3O_4 and Potassium aluminate.

Atmospheric nitrogen and hydrogen after being thoroughly purified and dried, are mixed in the ratio of 1 : 3 and compressed to 200 atmosphere pressure. The compressed mixture is then passed through a chamber which contains catalyst ($Fe_3O_4 + K_2O.AlO_2$) heated only once up to a temperature of 450°C. The reaction being exothermic, further heating is unnecessary. The gaseous mixture coming out of this chamber contains about 15–17% of ammonia which is passed through a spiral immersed in refrigerated brine, where ammonia is liquefied. The residual gases are mixed with more of nitrogen and hydrogen and are recirculated over the catalyst.



Cyanamide Process is also used for the large scale preparation of NH_3.

$$CaC_2 + N_2 \xrightarrow[100^\circ C]{\text{Electric arc}} CaCN_2 + C$$

$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$$

Halides:

The members of nitrogen family form two sets of halides MX_3 and MX_5. Nitrogen cannot form pentahalides as it has no "d" orbitals.

Trihalides:

Nitrogen forms a very stable, unreactive gaseous fluoride, NF_3. It also forms an unstable explosive liquid chloride, NCl_3. Pure tribromide and tri-iodide compounds are unknown.

Each of the other four elements form each of the four possible trihalides. They can be prepared by direct reaction of the elements in stoichiometric proportion, e.g.

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

The reactions are all exothermic.

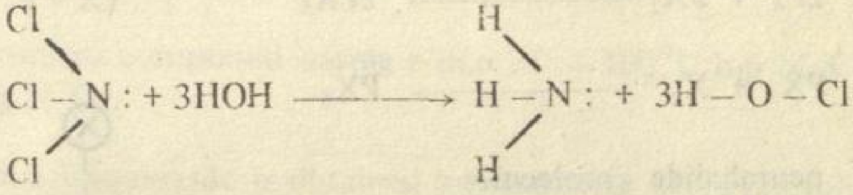
These trihalides are predominantly covalent and, like NH_3, have a tetrahedral structure with one position occupied by a lone pair. BiF_3 is, however, ionic in character. Increasing electropositivity of the elements towards the bottom of the group imparts ionic character to the bonding, and this is reflected in the increase in the melting and boiling points, as indicated in Table 7.4.

Table 7.4

Some physical properties of group V halides.

Trichlorides	M.P. (°C)	B.P. (°C)	Appearance
NCl_3	——	71	Yellow explosive oil
PCl_3	–92	76	colourless volatile liquid.
$AsCl_3$	–16	130	colourless liquid
$SbCl_3$	73	221	soft, colourless mass
$BiCl_3$	232	441	white solid..

Nitrogen trichloride is hydrolysed to form ammonia and hypochlorous acid. Co-ordination to a hydrogen of a water molecule occurs through the lone pair of electrons of the nitrogen atom, as shown below:



Since phosphorus, arsenic and antimony can expand their octet their trihalides hydrolyse readily, giving the appropriate oxy-acid of the Group V elements:

$$PCl_3 + 3H_2O \longrightarrow 3HCl + H_3PO_3$$

$$AsCl_3 + 3H_2O \longrightarrow 3HCl + As(OH)_3$$

The extent of hydrolysis diminshes as the metallic character of the Group V element increases.

With the exception of NCl_3 the trihalides have a tendency to act as electron 'acceptors' and can undergo addition reactions e.g.

$$SbCl_3 + \overline{Cl} \longrightarrow Sb\overline{Cl_4}$$

$$BiCl_3 + 2\overline{Cl} \longrightarrow BiCl_5^{-2}$$

PCl_3 reacts readily with oxygen to form the oxychloride, $POCl_3$. The molecule is tetrahedral. The oxidation state of phosphorus in this molecule is + 5.

Pantahalides:

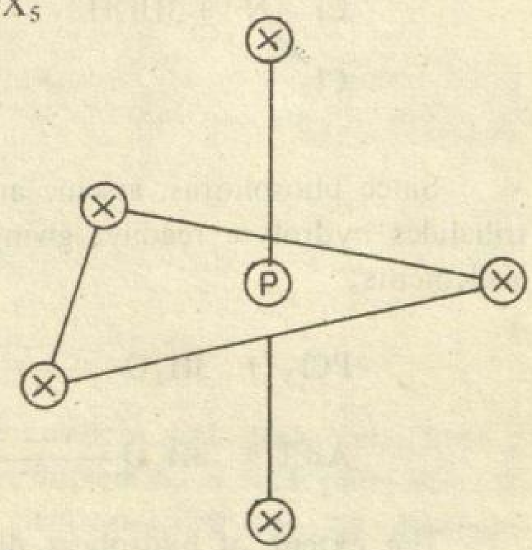
Nitrogen cannot form pentallhalides as it has no "d" orbitals. All the pentahalides of phosphorus, except the iodide, are known. It is apparently impossible for five large iodine atoms to fit around the relatively small phosphorus atom. Only four pentahalides of arsenic, antimony and bismuth are known. They are AsF_5, SbF_5, BiF_5, and $SbCl_5$.

The pentahalides are prepared either by direct reaction of excess halogen with the element, or by further reaction of the trihalide with the appropriate halogen:

$$2P_4 + 5X_2 \longrightarrow 2PX_5 \qquad (X = F,\ Cl,\ Br)$$

$$PX_3 + X_2 \longrightarrow PX_5$$

The pentahalide molecules have the trigonal bipyraimd structure in the gas phase as shown below:



Trigonal bipyramidal structure of pentahalides

The pentahalides are volatile materials, on heating they dissociate into trihalides and a molecule of halogen.

$$MX_5 \longrightarrow MX_3 + X_2$$

$$PCl_5 \longrightarrow PCl_3 + Cl_2$$

Hydrolysis of PCl_5 gives rise to oxychloride $POCl_3$.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$

but in excess water the following reaction producing orthophosphoric acid, H_3PO_4, is dominant:

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$

Oxides

The elements of group VA form two Chief sets of Oxides $(M_2O_3)_2$ and $(M_2O_5)_2$. Nitrogen is different; it forms five different Oxides.

Sesqui-Oxides:

$(M_2O_3)_2$ Oxidation state + 3:

Nitrogen sesquioxide or di-nitrogen trioxide is not formed by direct combination of the elements. It is prepared by cooling a mixture of NO and NO_2 at – 20°C

$$NO + NO_2 \longrightarrow N_2O_3$$

It is a covalent compound having a m.p of – 102°C, b.p of 3.5°C and has the formula N_2O_4.

Phosphorus sesquioxide is obtained by Oxidizing white phosphorus at about 100°C in a limited supply of air.

$$P_4 + 3O_2 \longrightarrow P_4O_6$$

It is a white crystalline solid which melts at 23.8°C and boils at 17.4°C. The molecular weight measurements show that it exists in the form of P_4O_6 molecules. Phosphorus trioxide is thus dimeric and should be written as P_4O_6.

When burnt in air, arsenic, antimony and bismuth are oxidized to sesquioxides. The sesquioxides of arsenic and antimony are assigned the formulas As_4O_6 and Sb_4O_6: Bismuth sesquioxide is not dimeric and is assigned the empirical formula Bi_2O_3. These sesquioxides are solids at ordinary temperatures. As_4O_6 and Sb_4O_6 being white and Bi_2O_3 yellow.

These sesquioxides show a clear trend from acidic to basic character down the Group:

N_2O_3	P_4O_6	As_4O_6	Sb_4O_6	Bi_2O_3
acidic	acidic	amphoteric	amphoteric	basic

Thus N_2O_3, P_4O_6 and As_4O_6 each react with water to form acids:

$$N_2O_3 + H_2O \longrightarrow 2HNO_2 \qquad \text{(nitrous acid)}$$

$$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3 \qquad \text{(phosphorous acid)}$$

$$As_4O_6 + 6H_2O \longrightarrow 4H_3AsO_3 \qquad \text{(arsenious acid)}$$

Whereas nitrogen and phosphorous sesquioxides have no basic properties arsenic sesquioxide dissolves more readily in HCl than it does in water.

$$As_4O_6 + 12HCl \longrightarrow 4AsCl_3 + 6H_2O$$

Antimony and bismuth sesquioxide are insoluble in water. Antimony sesquioxide is amphoteric, with basic character being much more pronounced than in the corresponding arsenic compound. Sb_2O_3 reacts with OH^- and H^+ ions to yield antimonite and antimonyl ions respectively?

$$Sb_2O_3 + 2OH^- \longrightarrow H_2O + 2SbO_2^-$$

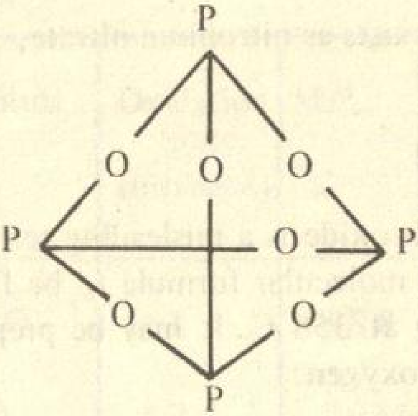
$$Sb_2O_3 + 2H^+ \longrightarrow H_2O + 2SbO^+$$

Bismuth trioxide is completely basic in character and is soluble in acids but insoluble in solutions of bases. The even greater metallic character of the Bi_2O_3 is entirely consistent with the fact that of all the elements in the Group bismuth has the largest atomic radius and lowest electronegativity.

Structure of Sesquioxides.

Vapour density determination shows that the molecular formula of phosphorus sesquioxide is P_4O_6. Electron diffraction studies have shown that the four phosphorus atoms form the tetrahedron as in white phosphorus. The six oxygens lie just outside the middle points of the six edges of the tetrahedron.

The structures of arsenic and antimony sesquioxides are similar to that of P_4O_6.



Pentoxide: Oxidation state +5

Tendency to attain +5 oxidation state decrease down the group. The pentoxides of all the members of nitrogen family are known. All of them are solids and all of them are acidic.

Nitrogen Pentoxide, N_2O_5. It is anhydride of nitric acid and is prepared by dehydrating HNO_3 with P_4O_{10} : $4HNO_3 + P_4O_{10} \longrightarrow 2N_2O_5 + 4HPO_3$

It is a white crystalline solid with m.p. 30°C. When heated rapidly, it explodes.

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

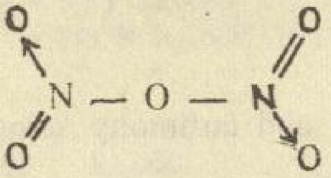
It reacts with alkalies:

$$2NaOH + N_2O_5 \longrightarrow 2NaNO_3 + H_2O$$

It dissolves in water with a hissing noise:

$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

In the gas phase, nitrogen pentoxide consists of simple N_2O_5 molecules and has the structure:



In the solid state, it exists as nitronium nitrate,

$$\overset{+}{NO_2}\,\overset{-}{NO_3}$$

Phosphorus pentoxide is a misleading term as vapour density measurements show the true molecular formula to be P_4O_{10}. It is a white deliquescent solid, subliming at 358°C. It may be prepared by burning phosphorus in an excess of air or oxygen:

$$4P + 5O_2 \longrightarrow P_4O_{10}$$

Phosphorus pentoxide is the anhydride of phosphoric acid.

The most important chemical characteristic of phosphoric anhydride is its tremendous affinity for water. This property makes the oxide one of the most useful drying agents. It reacts with water to form metaphosphoric acid, pyrophosphoric acid and finally orthophosphoric acid.

$$P_4O_{10} + H_2O \longrightarrow 2HPO_3 \xrightarrow{+H_2O} H_4P_2O_7 \xrightarrow{+H_2O} 2H_3PO_4$$

All of the pentoxides of group V elements are acidic in character. Whereas N_2O_5 and P_4O_{10} react readily with water to yield nitric acid and phosphoric acids, arsenic pentoxide dissolves slowly in water to give a solution of arsenic acid, H_3AsO_4. Antimony pentoxide is only sparingly soluble in water, but gives an acidic solution. No free antimonic acid derived from the oxide has been prepared, but antimonates containing $Sb(OH)_6^-$ are known. Bismuth pentoxide is insoluble. It does have acidic properties and alkaline bismuthates are known, e.g. sodium bismuthate, NaBiO.

N_2O is a colourless gas with pleasant taste and odour and when inhaled it produces hysterical laughter, hence the name laughing gas. It is fairly soluble in cold water . The solution of nitrous oxide in water is neutral. Materials that burn in air burn even more brightly in N_2O, because it contains 33% oxygen by volume as against the 21% in air e.g.

$$P_4 + N_2O \longrightarrow P_4O_{10} + 10N_2 .$$

Nitric oxide, NO : There are various ways of preparing NO :

(i) Heating Cu trunings with dil. HNO_3 ;

$$3Cu + 8HNO_3 \longrightarrow 2NO + 3Cu(NO_3)_2 + 4H_2O$$

(ii) By the reaction of $NaNO_2$ and KI in presence of H_2SO_4 pure NO is obtained :

$$2NaNO_2 + 3H_2SO_4 + 2KI \longrightarrow 2NaHSO_4 + K_2SO_4 + 2NO + I_2 + 2H_2$$

(iii) The gas is of commercial importance in the manufacture of nitric acid. The most important industrial method is the catalytic oxidation of ammonia :

$$4NH_3 + 5O_2 \xrightarrow[500^\circ C]{Pt} 4NO + 6H_2O$$

Nitric oxide can also be made by sparking nitrogen and oxygen (Birkeland-Eyde Process) :

$$N_2 + O_2 \xrightarrow{3000^\circ C} 2NO \quad \Delta H = +\ 43.2 \text{ Kcal}$$

This reaction is extremely endothermic.

The gas is colourless and relatively insoluble in water. It is neutral oxide and is not absorbed by alkalies.

1. The most important property of NO is that it is oxidized by atmospheric oxygen to NO_2 (brown-red), which then forms nitric acid and nitrous acid with water.

1. It is a brown paramagnetic gas. It forms a colourless dimer i.e., two molecules join up to form a single molecule. This is complete at – 11.2° After dimerization, paramagnetism disappears.

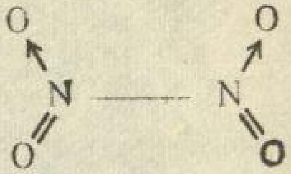
2. It dissolves in water to give nitric and nitrous acid. Therefore with alkalies it forms mixture of nitrites and nitrates.

3. It acts as an oxidising agent. It oxidizes Hydrogen sulphides to Sulphur and Sulphurous acid to Sulphuric acid

$$H_2S + NO_2 \longrightarrow H_2O + S + NO$$

$$SO_2 + H_2O + NO_2 \longrightarrow H_2SO_4 + NO$$

$$:\ddot{O}::\dot{N}:\ddot{O}: \longleftrightarrow :\ddot{O}:\dot{N}::\ddot{O}:$$



Oxyacids of Nitrogen Family

Corresponding to the two chief oxides M_2O_3 and M_2O_5, these elements form two series of acids. Those in which the oxidation state of M is +3 have– ous at the end of their names, while those in which the oxidation state of M is +5, are termed 'ic' acids.

$M_2O_3 + H_2O \longrightarrow 2HMO_2$, 'ous' acids oxidation No. + 3

$M_2O_5 + H_2O \longrightarrow 2HMO_3$ 'ic' acids oxidation No. + 5

The various oxyacids of nitrogen family are given in table 7.6.

Table 7.6

Ox. State	N	P	As	Sb	Bi
+ 3	HNO_2	H_3PO_3	H_3AsO_3	......	......
+ 5	HNO_3	H_3PO_4	H_3AsO_4	$HSb(OH)_6$	$HBiO_3$

Nitrous acid:

This is an unstable acid. It has not been isolated in the free state and it exists only in solution. The solution is blue in colour.

It can be prepared by dissolving N_2O_3 in cold water.

$$N_2O_3 + H_2O \longrightarrow 2HNO_2$$

It is also obtained when a nitrite is decomposed with dilute HCl or H_2SO_4 in cold.

$$NaNO_2 + HCl \longrightarrow NaCl + 2HNO_2$$

$$Ba(NO_2)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HNO_2$$

It decomposes even at low temperatures to nitric acid and nitric oxide.

$$2HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$$

It acts both as an oxidizing and a reducing agent. It oxidizes strong reducing agents like H_2S, HI, H_2SO_3 and is itself reduced to NO.

$$2HNO_2 + H_2S \longrightarrow S + 2H_2O + 2NO$$

Nitrous acid reduces strong oxidizing agents like acidified potassium permanganate and is itself oxidized to nitric acid.

$$2KMnO_4 + 3H_2SO_4 + 5HNO_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5HNO_3$$

Structure $\mathrm{H:\underset{..}{\overset{..}{O}}:\overset{..}{N}:\ \underset{..}{\overset{..}{O}}:}$ or $\mathrm{HO{-}N \rightarrow O}$

Phosphorous acid, H_3PO_3 : This can be made by hydrolysing P_4O_6, PCl_3, PBr_3 or PI_3 :

$$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$$

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

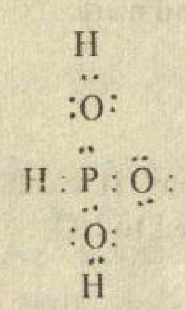
Phosphorus acid is a white crystalline, deliquescent solid. It has garlic-like odour.

It undergoes self oxidation reduction when its solution is warmed, Phosphine and phosphoric acid are formed.

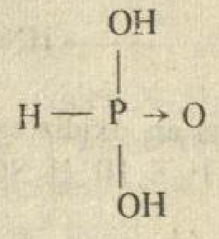
$$4H_3PO_3 \longrightarrow PH_3 + 3H_3PO_4$$

It is a dibasic acid and forms two series of salts.

H_3PO_3 is an active reducing agents, because it is easily oxidized to H_3PO_4. Although H_3PO_3 contains three hydrogen atoms per molecule, it is a diprotic, i.e. dibasic acid, because one of its hydrogens – the one linked directly with phosphorus, is not ionizable. Its electronic structure is given below:



$$\begin{array}{c} H \\ :\ddot{O}: \\ H:\ddot{P}:\ddot{O}: \\ :\ddot{O}: \\ H \end{array}$$



$$\begin{array}{c} OH \\ | \\ H-P\rightarrow O \\ | \\ OH \end{array}$$

Nitric Acid, HNO_3

Nitric acid is one of the most important chemicals for industrial use. It has been manufactured from $NaNO_3$ or KNO_3 since the days of alchemists. Now–a–days other methods for the manufacture of HNO_3 have been developed. Generally, the following methods are used for large-scale production of HNO_3.

(i) From nitrates: HNO_3 is produced commercially by heating a mixture of $NaNO_3$ and conc. H_2SO_4 in cast iron retorts to about 200°C when HNO_3 is distilled off:

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

(ii) From air (Arc process) : Air (which contains mainly N_2 and O_2) is subjected to high tension electric discharge or passed through an arc at a temperature of above 3000°C. N_2 and O_2 combines to give NO :

$$N_2 + O_2 \longrightarrow 2NO \quad \Delta H = 43.2 \text{ K Cal}$$

The reaction is endothermic and gives only about 5% conversion at 3000°C. On cooling NO combines with more O_2 to form NO_2 which then combines with water to give nitric acid

$$2NO + O_2 \longrightarrow 2NO_2$$

$$4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$$

This is one of the processes for the fixation of atmospheric nitrogen. The high cost of electricity and low yield of HNO_3 has led to the discontinuation of the process.

(iii) From ammonia (Ostwald's Process) : This process consists of the oxidation of ammonia to NO and NO to NO_2 which with water gives HNO_3. Ammonia mixed with 10 times its volume of air and heated to 600°C is passed through a converter containing platinum gauze which acts as a catalyst. NH_3 is oxidized to NO :

$$4NH_3 + 5O_2 \xrightarrow[600^\circ C]{Pt} 4NO + 6H_2O \quad \Delta H = -215 \text{ K cal.}$$

The exothermic reaction proceeds without supply of heat except the initial heating. About 90% of NH_3 is converted to NO. Additional air is admitted to cool the mixture and oxidize NO to NO_2 :

$$2NO + O_2 \longrightarrow 2NO_2 + 27.8 \text{ Kcal}$$

The mixed gases containing NO, NO_2, unreacted N_2 and O_2 etc. are passed in an absorption tower where HNO_3 is formed :

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

NO is returned to absorption tower with more air.

Properties :

Pure nitric acid is a colourless liquid which boil at 83°C and freezes to a white solid at – 41°C. It is miscible with water in all proportion.

Nitric acid exhibits three types of properties :

1. Acid properties.
2. Oxidizing agent.
3. Nitrating agent.

1. Acid properties. Nitric acid in dilute aqueous solution possesses a sour taste, turns blue litmus red. neutralizes alkalies decomposes carbonates and attacks various metals. Action of Nitric acid on metals is that of an acid and an oxidizing agent and thus becomes complicated.

(i) With alkalies.

$$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$$

(ii) With carbonates.

$$Na_2CO_3 + 2HNO_3 \longrightarrow 2NaNO_3 + CO_2 + H_2O$$

(iii) With metals.

$$Mg + 2HNO_3 \longrightarrow Mg(NO_3)_2 + H_2$$

2. As oxidizing agent : In consequence of the large proportion of Oxygen in Nitric acid and of the ease with which it is decomposed to give Oxygen, it behaves as a powerful oxidizing agent.

$$2HNO_3 \longrightarrow 2NO_2 + H_2O + O$$

(a) Action of HNO_3 on non-metals: Non-metals, such as S, C, I_2, P etc. are oxidized by concentrated HNO_3 in the hot condition evolving NO_2 and the oxyacids or oxides of the non-metals:

$$C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$$

$$S + 4HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$$

$$P + 5HNO_3 \longrightarrow H_3PO_4 + 10NO_2 + H_2O$$

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

(b) Action of HNO_3 on metals : Nearly all metals are attacked by nitric acid. The action is complex and the nature of the products depends (i) on the concentration of nitric acid, (ii) the nature of the reducing agent and (iii) the temperature.

In dilute solution with possibly Mg and Mn only, HNO_3 behaves as an acid liberating H_2. But with other metals the oxidizing actions predominate. Au and Pt do not react with HNO_3 under any condition, while certain metals, such as Fe, Al and Cr become "passive" due to the formation of a protective coating of metal oxide. Although the reduction products may be a mixture of nitrogen compounds, but for the sake of simplicity the following points may be remembered for writing the equations. HNO_3 in extremely dilute solutions gives NH_3 (Change of oxidation number of N from +5 to –3).

HNO_3 in very dilute solutions gives N_2O (Change of oxidation number of N from + 5 to + 1).

HNO_3 in dilute solutions gives NO (Change of oxidation number of N from +5 to + 2).

HNO_3 in concentrated solution and hot condition gives NO_2 (Change of oxidation number of N from +5 to +4);

Thus,

(i) Zn, Fe and Sn with extremely dilute HNO_3 in the cold giv NH_3 which combines with excess HNO_3 to form NH_4NO_3 :

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + 3H_2O + NH_4NO_3$$

$$4Sn + 10HNO_3 \longrightarrow 4Sn(NO_3)_2 + 3H_2O + NH_4NO_3$$

(ii) Zn reacts with very dilute HNO_3 in the cold to give N_2O

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

(iii) In the ordinary conditions the dilute HNO_3 always produces NO. This is the most common reaction product of HNO_3 with metals in dilute conditions (moderately). Metals such as Cu, Fe, Ag, Hg, etc. give similar reactions

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

(iv) In concentrated and hot condition most metals reacts with HNO_3 to give NO_2 :

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

$$Fe + 6HNO_3 \longrightarrow Fe(NO_3)_3 + 3NO_2 + 3H_2O$$

$$Sn + 4HNO_3 \longrightarrow H_2SnO_3 + H_2O + 4NO_2$$

(v) A mixture of one part by volume of concentrated nitric acid and three parts by volume of concentrated hydrochloric acid is called Aqua Regia (Royal water)

$$HNO_3 + 3HCl \longrightarrow Cl_2 + NOCl + 2H_2O$$

It dissolves such noble metals as gold and platinum which are inactive in either of the acids alone. The extra solvent power is the result of complex ion formation, e.g.

$$Au + 4H^+ + 4Cl^- + NO_3^- \longrightarrow AuCl_4^- + NO + 2H_2O$$

(c) Action on reducing agents. A number of strong reducing agents such as HI, HBr, H_2S, ferrous salts, etc., are oxidised by the nitric acid.

(i) $2HI + 2HNO_3 \longrightarrow I_2 + 2H_2O + 2NO_2$

(ii) $2HBr + 2HNO_3 \longrightarrow Br_2 + 2H_2O + 2NO_2$

(iii) $3H_2S + 2HNO_3 \longrightarrow 3S + 4H_2O + 2NO$

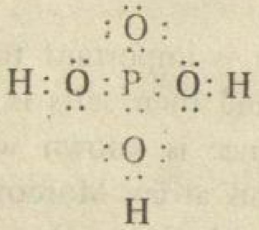
$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

It is also obtained commercially by treating calcium phosphate in phosphate rock with 60% sulphuric acid.

$$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3CaSO_4 + 2H_3PO_4$$

The insoluble calcium sulphate is filtered off, and the solution is concentrated to about 85% phosphoric acid by evaporation.

Pure ortho-phosphoric acid is a deliquescent white solid with melting point 42°C. It is a triprotic acid and is assigned the following electronic configuration :



$$\begin{array}{c} :\ddot{O}: \\ H:\ddot{O}:P:\ddot{O}:H \\ :\ddot{O}: \\ H \end{array}$$

It may be noted carefully that the hydrogen atoms in —OH groups are ionizable and therefore acidic, but the P – H bonds in phosphorus acids have reducing, not acidic properties. The PO_4^{-3} ion is tetrahedral in structure (compare SO_4^{-2} and CrO_4^{-2}.

The acid ionizes in three steps which are :

(1) $H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$; $K_1 = 1.1 \times 10^{-2}$ mole/litre

(2) $H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{-2}$; $K_2 = 7.5 \times 10^{-8}$ mole/litre

(3) $HPO_4^{-2} + H_2O \rightleftharpoons H_3O^+ + PO_4^{-3}$; $K_3 = 4.8 \times 10^{-12}$ mole/litre

The first ionization constant shows that the ortho phosphoric acid is only a moderately strong acid. When treated with bases, it forms three series of salts, for example NaH_2PO_4, Na_2HPO_4 and Na_3PO_4.

(1) $H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$

(2) $NaH_2PO_4 + NaOH \longrightarrow Na_2HPO_4 + H_2O$

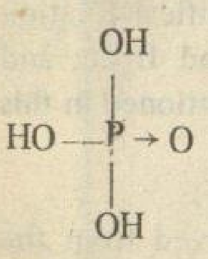
(3) $Na_2HPO_4 + NaOH \longrightarrow Na_3PO_4 + H_2O$

Sodium dihydrogen phosphate, NaH_2PO_4 is weakly acidic. It is used in baking powder. Disodium phosphate, Na_2HPO_4 is slightly basic. Trisodium phosphate, Na_3PO_4, also called the normal sodium phosphate is strongly basic. It is used extensively as a water softener (for treating water boiler) and as a cleansing agent.

Ortho-phosphoric acid loses water on heating and is converted to pyrophosphoric acid. The pyrophosphoric acid loses water again and is converted to meta-phosphoric acid.

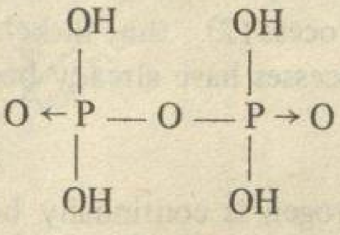
$$2H_3PO_4 \xrightarrow[216^\circ C]{-H_2O} H_4P_2O_7 \xrightarrow[\text{red heat}]{-H_2O} 2HPO_3$$

The various phosphoric acids have the following structures.



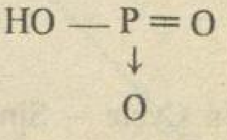
$HO-\overset{OH}{\underset{OH}{P}}\rightarrow O$

(ortho)



$O\leftarrow\overset{OH}{\underset{OH}{P}}-O-\overset{OH}{\underset{OH}{P}}\rightarrow O$

(Pyro)



$HO-\underset{\substack{\downarrow\\ O}}{P}=O$

(meta)

Fixation of Nitrogen – Animals and plants require nitrogen in order to maintain life. Since they cannot use free nitrogen, they get their supply in the form of nitrogen compounds. The conversion of chemically unreactive elementary nitrogen into more reactive compounds is called 'nitrogen fixation'.

Nitrogen compounds are essential to all living organisms for the formation of proteins, which are complicated organic compounds containing carbon, hydrogen, oxygen, nitrogen, and sometimes phophorus and sulphur.

Animals must take proteins directly, as the body is incapable of builiding up proteins from other nitrogen compounds. On the other hand plants can synthesize proteins from ammonium or nitrate salts, which they derive from the soil. The soil gets nitrogen compounds from the decay of plants, leaves and other organic matter.

Methods for the fixation of nitrogen may be divided into two groups:
(1) Natural fixation, and (2) Artificial fixation.

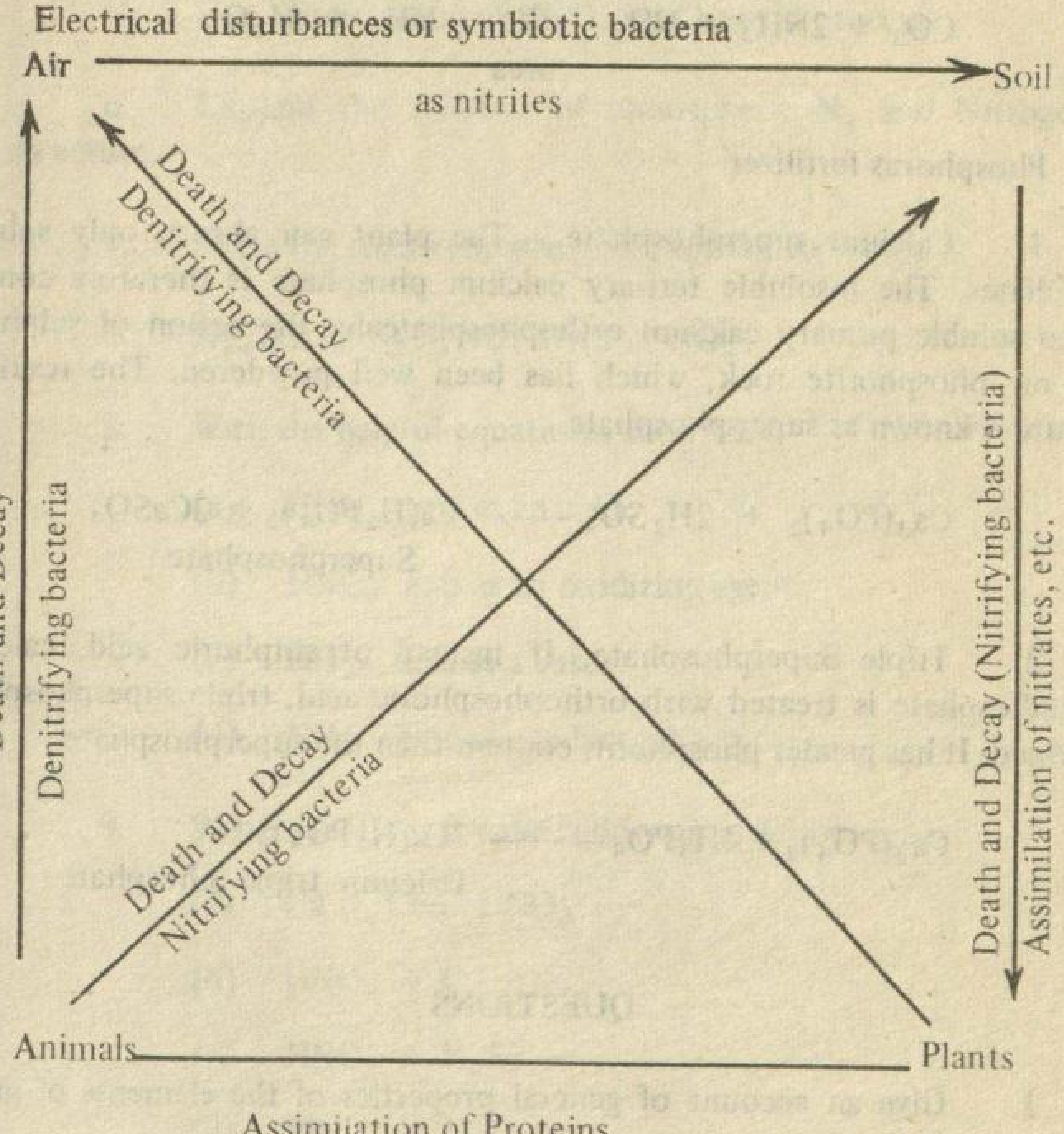
Natural Fixation – 1. Certain plants such as peas, beans, alfalfa, called legumes, maintain a co-operative relationship with certain kinds of nitrogen-fixing bacteria. These bacteria, which are found on the root nodules of the leguminous plants, are able to absorb free nitrogen directly from the atmosphere and convert it into nitrogen compounds.

(2) Another method of replenishing the supply of nitrogen compounds in the soil is based on elelctrical discharges of lightening, which cause the nitrogen and oxygen of the atmosphere to unite. The oxides of nitrogen, thus produced, combine with the moisture to form nitrous and nitric acids which are carried down to the soil by rain.

Artificial Fixation – The important methods for artifical fixation of nitrogen are (1) the Haber's Process (2) the Birkeland and Eyde; and (3) the Cyanamide. These processes have already been mentioned in this Chapter.

Nitrogen Cycle – Since nitrogen is continually being fixed from the atmosphere by both natural and artificial processes, it may appear as if the supply of nitrogen in the air is decreasing. But this is not true. The percentage of nitrogen in the atmosphere remains almost constant because a balance between free and combined nitrogen is maintained owing to the decomposition of nitrogen compounds, giving elemental nitrogen.

The atmospheric nitrogen goes into the soil as nitrites and nitrates by electric disturbances through symbiotic bacteria These slats are assimilated by plants. The animals take the plants as their food, and nitrogen present in plants in the form of proteins is transferred to animals. Some of the plants may decay and nitrogen from them goes back to air by denitrifying bacteria. The soil also again gets nitrogen from the decaying plants by nitrifying bacteria. When animals excrete urine or die, the nitrogen goes to the soil by nitrifying bacteria and to the air by denitrifying bacteria Thus a cycle of nitrogen is going on in nature. Diagrammatically the nitrogen cycle in nature may be shown as follows :-


Electrical disturbances or symbiotic bacteria
Air
Soil
as nitrites
Death and Decay
Denitrifying bacteria
Death and Decay
Denitrifying bacteria
Death and Decay
Nitrifying bacteria
Death and Decay (Nitrifying bacteria)
Assimilation of nitrates, etc.
Animals
Plants
Assimilation of Proteins

Nitrogenous Fertilizer : Plants need nitrogenous compounds for their nourishment. They can absorb substances only in solution. The soluble nitrogen compounds which are mostly used as fertilizers are (1) Ammonium sulphate (2) Urea.

Ammonium sulphate is produced by neutralizing crude chamber sulphuric acid with ammonia produced by Haber's process.

Urea is manufactured synthetically by the action of carbon dioxide on ammonia in an autoclave.

$$CO_2 + 2NH_3 \rightarrow \underbrace{NH_2 - CO - NH_2}_{\text{urea}} + H_2O$$

Phosphorus fertilizer

1. Calcium superphosphate. The plant can absorb only soluble phosphates. The insoluble tertiary calcium phosphate is therefore converted to soluble primary calcium orthophosphate by the action of sulphuric acid on phosphorite rock, which has been well powdered. The resulting mixture is known as super-phosphate.

$$Ca_3(PO_4)_2 + 2H_2SO_4 \longrightarrow \underbrace{Ca(H_2PO_4)_2 + 2CaSO_4}_{\text{Superphosphate}}$$

2. Triple Superphosphate. If instead of sulphuric acid, calcium orthophosphate is treated with orthophosphoric acid, triple superphosphate is formed. It has greater phosphorus content than the superphosphate.

$$Ca_3(PO_4)_2 + 4H_3PO_4 \longrightarrow \underset{\text{Calcium triple phosphate.}}{3Ca(H_2PO_4)_2}$$

QUESTIONS

1. Give an account of general properties of the elements of group VA.

2. Three unmarked cylinders contain N_2O, NO_2 and NH_3. How could you identify each one of them.

3. By means of equations show how the following conversions can be brought about (a) $P \rightarrow H_3PO_4$ (b) $N_2 \rightarrow NH_3$ (c) $N_2 \rightarrow N_2O$ (d) $N_2 \rightarrow NO_2$.

4. Explain with equations, the effect of heat on (a) NH_4HCO_3 (b) NH_4NO_2, (c) NH_4NO_3 (d) NH_4Cl (e) $Pb(NO_3)_2$ (f) KNO_2.

5. Discuss the Chemistry of

(i) The manufacture of NH_3 by Haber process.

(ii) Preparation of HNO_3 by Ostwald process.

6. Explain the fixation of atmospheric N_2 and Nitrogen cycle in nature.

7. Write the electronic structures for the following :

H_2, $\overset{+}{NH_4}$, N_2O, NO, HNO_3, NO_2^-.

8. With the help of equations, show that —

(a) HNO_3 acts as an acid.

(b) HNO_3 acts as an oxidizing agent.

(c) NH_3 acts as a base.

(d) NH_3 acts as a reductant

9. Write equations for the following reactions.

(a) $Cu + \text{Con. } HNO_3 \rightarrow$

(b) $HNO_3 + C \rightarrow$

(c) $HNO_3 + H_2S \rightarrow$

(d) $PBr_3 + H_2O \rightarrow$

(e) $SbCl_3 + H_2O \rightarrow$

(f) $P_4O_{10} + C \rightarrow$

(g) $As_4O_6 + H_2 \rightarrow$

(h) $NH_3 + O_2 \rightarrow$

10. Discuss the action of HNO_3 on metals. What is the basis of the ring test for NO_3^- ion.

CHAPTER 8

GROUP VI A ELEMENTS

THE OXYGEN FAMILY

Group VI A of the periodic table consists of Oxygen, Sulphur, Selenium, Telurium and Polonium.

The first four elements are non-metallic in character and are collectively known as Chalcogens or ore forming elements. Most of the metallic ores are either oxides or sulphides. Selenium and Telurium show weaker non-metallic character while Polonium is typically metallic. Polonium is radioactive and short lived and is found very rarely, therefore it will not be discussed here in details.

Electronic Configuration and Position in the Periodic Table.

The elements have been placed in the 6th group of the periodic table because all of them contain six electrons in the valence shell as shown in the Table 8.1.

Table 8.1

Element	Symbol	At. No. (Z)	Electronic configuration.	Oxidation states
Oxygen	O	8	[He] $2S^2 2P^4$	-2
Sulphur	S	16	[Ne] $3S^2 3P^4$	-2 $+4$ $+6$
Selenium	Se	34	[Ar] $3d^{10} 4S^2 4P^4$	-2 $+4$ $+6$
Telurium	Te	52	[Kr] $4d^{10} 5S^2 5P^4$	-2 $+4$ $+6$
Polonium	Po	84	[Xe] $4f^{14} 5d^{10} 6S^2 6P^4$	-2 $+4$ $+6$

It can be seen from the above table that each element has $S^2 P^4$ electronic configuration in the valence shell. Each element is short of 2 electrons and tends to attain the inert gas configuration either by gaining or sharing two electrons.

In most of their common compounds these elements show the oxidation state of -2 .

General Characteristics : These elements show group similarities, although Oxygen differs in some respects from the rest of the elements. There is a gradual change in properties within the group.

Some of the important properties of these elements are given in the Table 8.2.

Table 8.2

Element	At. No. Z	At. Wt	At. Radius A°	M.Pt.	B.Pt.	I. P.	Electronegativity.
O	8	15.994	0.74	–219	–183	13.61	3.5
S	16	32.064	1.04	119	444.6	10.36	2.5
Se	34	78.96	1.17	217.4	684.8	9.75	2.4
Te	52	127.96	1.37	450	1390	9.01	2.1
Po	84	210.0	1.52	=	=	8.43	2.0

It can be seen from the above table that these elements show a regular trend in most of their properties

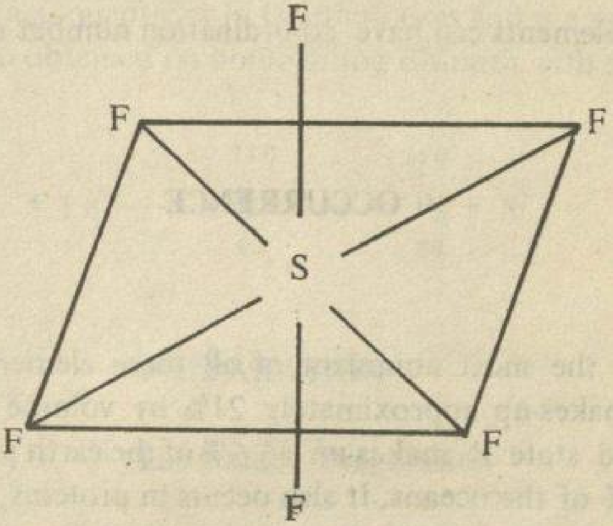
1. The melting point, B.Pt, At. radius and density increase down the group. This is due to the fact that as the At. No is increased, the atomic radius also increases and therefore, Van der Waals forces will also increase. Thus much energy is required to separate the atoms in the metallic crystal lattice as the At. No. is increased.

2. Ionisation potential and electro-negativity decrease down the group as the At. No. is increased.

3. The Electro-negativity of Oxygen suggests that most of the metal oxides will be ionic and contain oxide ions, O^{-2}. Oxygen shows oxidation state of -2 in its common compound, but oxidation state of -1 in peroxides. S, Se, Te form few compounds which are more than 50% ionic even with the most electropositive elements. Thus S^{-2}, Se^{-2}, and Te^{-2} ions are less probable.

When bonded to a more clctro-negative element, these elements show oxidation states of +2 for example in (OF_2) oxygen shows oxidation state of +2. Oxygen is always divalent because its valence shell (2nd shell) is limited to a maximum of 8 electrons. However, the elements S, Se, Te and Po can show oxidation state of +4 and +6 because each one of them has empty d-orbitals available for bonding.

The best known compounds of S, Se, Te with Oxygen are typically tetravalent but with Fluorine, they form hexavalent compounds e.g. SF_6 having an oxidation state of +6. The higher oxidation states become less stable down the group. The compounds in which these elements have oxidation state of +4 show both oxidation and reducing properties. For example in SO_2 sulphur shows oxidation state of +4 and it shows oxidizing as well as reducing properties.



In the +6 oxidation state the compounds are only oxidizing and typically volatile because they are covalent in natue.

4. The decrease in the ionization potential down the group suggests that the electrons are less firmly bonded in the larger atoms. Consequently the metallic character increases as the atomic number of element is increased. Thus Oxygen and sulphur are typically non-metallic, Se and Te show weaker non-metallic character, while Po is a metal.

1. **Sulphide ores:** $CuFeS_2$, Cu_2S, PbS, As_2S_3, Sb_2S_3, Bi_2S_3.

2. **Sulphate ores:** $CuSO_4 . 5H_2O$, $SrSO_4$, $BaSO_4$, (Byrite), $CaSO_4 . 2H_2O$, $MgSO_4 . 7H_2O$ (Epsom salt) and $Na_2SO_4 . 10H_2O$ (Glauber salt).

It also occurs in the combined state in plants such as garlic, onion and in animal life. Petroleum also contains some sulphur.

Selenium Telurium and Polonium :

Se and Te are generally obtained from the anode sludge (or mud) during the electrolytic refining of copper in the copper sulphate solution.

They occur as selenides and tellurides in sulphide ores of heavy metals.

Po occurs in trace quantities in Uranium ores and is a product of radioactive decay. It is also obtained on bombarding Bismuth with neutrons.

$$^{209}_{83}Bi + 1n^{\circ} \longrightarrow {}^{210}_{83}Bi \longrightarrow {}^{210}_{84}P_0 + 1e^{-}$$

PREPARATION

1. Laboratory Preparation

Oxygen :

(a) It is prepared by heating a mixture of potassium chlorate ($KClO_3$) and Manganese Dioxide (MnO_2) in the ratio of 4 : 1, in a hard glass tube fitted with a delivery tube which passes through water.

$$2KClO_3 + MnO_2 \longrightarrow 2KCl + 3O_2 + MnO_2$$

MnO_2 is used as a catalyst which accelerates rate of the reaction. The gas is collected over water.

(b) It is also prepared by the reaction between water and sodium Perxide.

$$2Na_2O_2 + 2H_2O \longrightarrow 4NaOH + O_2$$

2. Commercial Preparation

On large scale it is most economically obtained from liquid air and water.

(a) **From liquid air :** Liquid air is a mixture of liquid oxygen, liquid Nitrogen and liquid noble gases. These liquefied gases possess different boiling points. Therefore advantage can be taken of the difference in their boiling points and they can be fractionally separated.

On fractional disillation, Nitrogen being more volatile (B.Pt. – 195°C) than oxygen (B.pt. –182.5°C), distills first leaving the liquid, rich in oxygen. By continuous distillation oxygen can be recovered from the liquid air.

(b) **From water :** Where electric supply is cheaper, it is obtained by the electrolysis of water containing some quantity of mineral acids or alkalies.

Sulphur :

It is brought to the surface in the molten form by first forcing down steam and water at a temperature of 170°C and a pressure of 100 lb per sq in. and then pumping down hot compressed air.

Allotropy :

Oxygen occurs in two non-metallic allotropic forms or modifications–O_2 and O_3 (Ozone).

Sulphur exists in two crystalline forms Rhombic Sulphur or α sulphur which is stable at room temperature, and monoclinic sulphur or β-sulphur which is stable above 95.5°C. Plastic or amorphous sulphur can be obtained by pouring molten sulphur into water. All these forms of sulphur are non-metallic in character. Selenium exists as a non-metallic form (red) and a metallic form (grey). Tellurium has also two allotropic forms: metallic and non-metallic, the former being more stable than the latter. Thus, as explained earlier, there is a gradual increase in metallic character down the group.

Molecular structure of Group VI Elements :

Oxygen is stable as a di-atomic molecule which accounts for its being a gas.

However S, Se, Te and Po are solids at ordinary temperature and have more complex molecules. S and Se exist as S_8 and Se_8 molecules at room temperature. They have ring structures (Fig. 8.1).

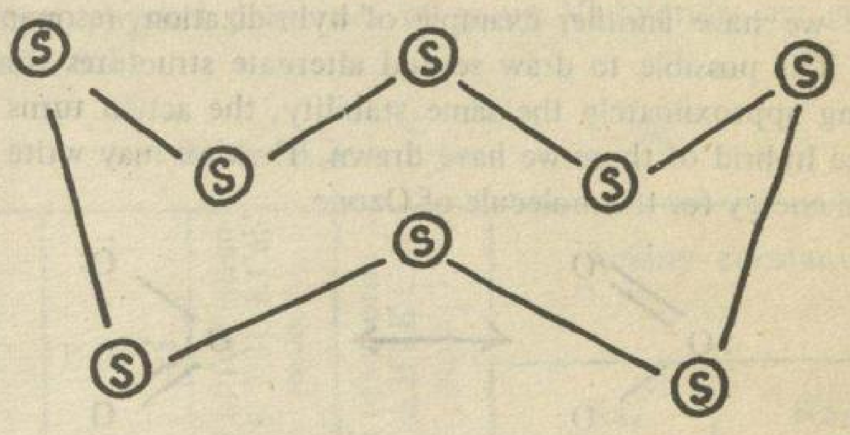
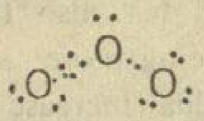


Fig. 8.1 : Structure of Sulphur molecule, S_8

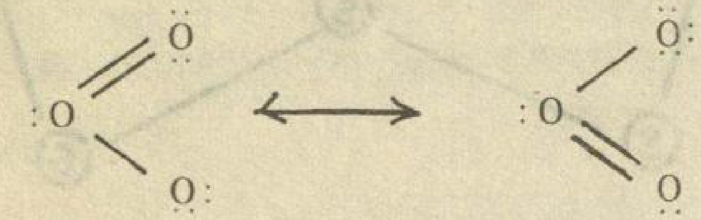
Such type of rings are known as pukered rings.

The bonding in oxygen molecule is not so simple as might appear at first. If the molecule is considered to have two covalent bonds as

$:\ddot{O}:\ :\ddot{O}:$ or $O = O$, then all the electrons would be paired and the molecule would be diamagnetic. But it has been proved that oxygen molecule is paramagnetic *i.e.*, it contains unpaired electrons. The molecular orbital theory predicts the paramagnetic molecular structure for oxygen.



The molecular structure of ozone is V–shaped and is represented by indicating that middle oxygen atom is linked by a double bond to one and a dative bond to the other oxygen atom. Here again a complication arises. The properties of O_3 indicate that the two bonds are exactly alike. A normal bonding for a single covalent bond between two oxygen atoms is 1.48A° and for a double bond it is 1.10A°. But the bond length in O_3 is 1.26A° which has intermediate value between single and double bond lengths. We have learnt that bonds of hybrid S and P orbitals exist in many molecules. Here we have another example of hybridization, resonance hybrid. Whenever it is possible to draw several alternate structures for a molecule, each having approximately the same stability, the actual turns out to be a resonance hybrid of those we have drawn. Thus we may write two structures of equal energy for the molecule of Ozone.



The actual structure is neither of the two, nor does it alternate between them as the term resonance might suggest. It is hybrid of the two structures with less energy and therefore more stability than either.

All these elements combine with hydrogen forming hydrides.

$H_2O, H_2S, H_2Se, H_2Te, H_2Po$

Oxygen forms two hydrides H_2O and H_2O_2.

Hydrogen Sulphide: (H_2S)

It is prepared by the decomposition of metallic sulphides with dilute acids. In laboratory it is prepared by the action of dil. H_2SO_4 on ferrous-sulphide in the Kipps generator.

$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S \uparrow$$

2. H_2Se and H_2Te are prepared by the action of dilute acid on metallic selenides and tellurides respectively. For example :

$$CuSe + H_2SO_4 \longrightarrow CuSO_4 + H_2Se$$

$$CuTe + H_2SO_4 \longrightarrow CuSO_4 + H_2Te$$

General Characteristics of the hydrides

These hydrides with the exception of H_2O are colourless, poisonous and unpleasant smelling gases. Water is liquid at ordinary temperature.

Some important physical properties of group VI hydrides are given in the following Table 8.3 :

Table. 8.3.

Hydrides	M.Pt°C	B.Pt °C	Heat of formation ΔH_f at 25°C K Cal/ mole	Heat of vaporisation ΔHv K Cal/ mole	Acidity constant	
					Ka_1 moles/litre	Ka_2 moles/litre
H_2O	0.00	100.00	–6.835	9.715	1.00×10^{-14}	above 10^{-20}
H_2S	–85.6	–60.75	–4.82	4.463	1×10^{-7}	10^{-15}
H_2Se	–60.4	–41.5	+ 8.2	+ 4.75	2×10^{-4}	above 10^{-10}
H_2Te	–51.00	–1.8	23.8	5.7	2×10^{-3}	above 10^{-3}

From the above table it can be seen that water shows somewhat different behaviour from the rest of the hydrides.

The melting point and boiling point of water is high; these values decrease from water to H_2S and then increase. As already explained, in water molecule, oxygen atom is more electronegative, which attracts the shared pair of electrons from Hydrogen atom. This makes hydrogen atom partially positively charged and oxygen atom partially negatively charged. The water molecule thus developes polar character. The polar molecules of water then attracts each other due to opposite charge and strong hydrogen bonds are formed. Due to strong hydrogen bonding, the water molecules are highly associated and clusters of molecules are formed. It, therefore, requires much energy to separate or dissociate the water molecules.

The chemical properties of these hydrides can also be explained with the help of the above table.

The thermal stability decreases in the order.

$$H_2O > H_2S > H_2Se > H_2Te$$

This is due to decreasing heat of formation from H_2O to H_2Te.

At 2000°C only four percent of water is decomposed to hydrogen and oxygen while H_2Se and H_2Te are decomposed even at room temperature.

The acidity constant of these hydrides increases down the group. These values show that they act as weak diprotic or dibasic acids.

The acid character increases in the order :

$$H_2O < H_2S < H_2Se < H_2Te$$

H_2S is a stronger acid than water because it readily ionises in aqeous solution *e.g.*,

$$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$$

$$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{--}$$

It therefore neutralizes alkalies forming two series of salts, acid-sulphide (Bi–sulphide) and normal sulphide.

$$H_2S + NaOH \rightarrow NaHS + H_2O$$

Sodium acid sulphide

$$NaHS + NaOH \rightarrow Na_2S + H_2O$$

Sodium sulphide

These hydrides are reducing agents and the reducing power increases down the group, due to their decreasing stability. The aqueous solution of H_2S and H_2Se are slowly oxidized by air.

$$H_2S + \frac{1}{2} O_2 \rightarrow H_2O + S$$

$$H_2Se + \frac{1}{2} O_2 \rightarrow H_2O + Se$$

H_2S is a strong reducing agent. It reduces halogens, acidified $KMnO_4$, $K_2Cr_2O_7$, Ferric salts, and iodine,

$$H_2S + I_2 \rightarrow 2HI + S$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2S \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$$

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$

$$H_2O_2 + H_2S \rightarrow 2H_2O + S$$

$$H_2S + 2FeCl_3 \rightarrow 2FeCl_2 + 2HCl + S$$

When any oxidizing agent like HNO_3 or H_2SO_4, reacts with H_2S, yellow precipitate of sulphur is formed which shows the presence of sulphur in H_2S.

$$H_2S + 2HNO_3 \rightarrow 2NO_2 + 2H_2O + S$$

$$H_2S + H_2SO_4 \rightarrow 2H_2O + SO_2 + S$$

The precipitation of metallic sulphides by H_2S is commonly used in qualitative analytical procedures as a step in the separation of the various cations. As is indicated by the equilibrium :

$$H_2S \rightleftharpoons 2\overset{+}{H} + \overset{--}{S}$$

Careful control of the H^+ ions concentration can be used to hold the sulphide ions concentration in a solution saturated with H_2S at such a value that the solubility product of the less soluble sulphides are exceeded, so that these substances are precipitated more while the soluble sulphides remain in solution. Thus sulphides of the II group cations of the qualitative analysis are precipitated in acid medium and those of fourth group cations in the alkaline medium.

$$Cu^{2+} + H_2S \rightarrow CuS + 2H^+$$

(Acidic medium)

$$Zn^{2+} + H_2S \rightarrow ZnS + 2H^+$$

(Alkaline medium)

OXIDES

Since oxygen is the second most electronegative element, it forms compounds with metals as well as non-metals. Its compounds with metals are essentially ionic solids. The crystals of metal oxides are made up of metallic ions and oxide ions. The oxides of the more electronegative non-metals are usually gases containing covalently linked oxygen atoms. Oxides of elements near the middle groups of the periodic table are usually found as giant molecules. Silicon dioxide (SiO_2) is a giant, three dimensional net work of Si-O-Si bonds. As would be expected, the ionic oxides have high melting points whereas the covalent oxides, unless they possess network structure as in SiO_2 are usually volatile.

CLASSIFICATION OF OXIDES

Oxides are generally classified as under :

1. **The Basic Oxides** : These are the oxides of metals. They are ionic in nature. Basic oxides of the alkali metals, the alkaline earth metals and of a few transition metals are soluble in water. They react with water giving the corresponding metal hydroxide (alkali).

$$Na_2O + H_2O \rightarrow 2NaOH$$

$$CaO + H_2O \rightarrow Ca(OH)_2$$

They are known as basic anhydrides. The other metal oxides are water insoluble.

2. **The Acidic Oxides** : These are usually oxides of non-metals. Since only fluorine is more electronegative than oxygen, its oxidation number in oxygen fluoride (OF_2) is -1 and that of oxygen is $+2$. In all other oxides the non-metal is in a positive oxidation state.

Such oxides are usually made up of small molecules and are gases under ordinary conditions. When dissolved in water they form acids e.g.,

$$SO_2 + H_2O \rightarrow H_2SO_3$$
$$CO_2 + H_2O \rightarrow H_2CO_3$$
$$P_2O_5 + H_2O \rightarrow 2HPO_3$$
$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

They are known as acidic anhydrides.

Some heavy metals like Cr, Mn, Sn also give acidic oxides viz Cr_2O_3, Mn_2O_7, SnO_2 which when dissolved in water give respective acids.

$$Cr_2O_3 + H_2O \rightarrow H_2CrO_4$$
(Chromic caid)

$$Mn_2O_7 + H_2O \rightarrow 2HMnO_4$$
(Permanganic caid)

$$SnO_2 + H_2O \rightarrow H_2SnO_3$$
(Stannic acid)

3. **Amphoteric Oxides** : Certain metals like Al, Zn, and Sn give oxides which behave both as acidic oxides as well as basic oxides. Such oxides are called Amphoteric oxides. They react with both acids and bases forming salts and water e.g.

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$
$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$$
(Sod. aluminate)

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$$

$$ZnO + 2NaOH \rightarrow \underset{\text{(Sod. zincate)}}{Na_2ZnO_2} + H_2O$$

$$SnO_2 + 2HCl \rightarrow SnCl_2 + 2H_2O$$

$$SnO_2 + 2NaOH \rightarrow \underset{\text{(Sod. stannite)}}{Na_2SnO_2} + H_2O$$

4. **Neutral Oxides** : These are generally oxides of non-metals which show neither acidic nor basic character. For example CO, N_2O, NO, H_2O. They are insoluble in water. Although water is considered as a neutral oxide, it should more correctly be treated as amphoteric hydroxide, H(OH).

5. **Peroxides** : These are oxides which contain more oxygen than required by the element in the normal oxides. In these oxides oxygen has an oxidation state of – 1. They involve O – O bonds as well as M – O bonds but no M – M bonds, for example :

H_2O_2 or (H–O–O–H). Na_2O_2, BaO_2. These oxides when treated with water or acids give hydrogen peroxides . e.g.,

$$Na_2O_2 + 2H_2O \rightarrow 2NaOH + H_2O_2$$

$$Na_2O_2 + 2HCl \rightarrow 2NaCl \quad + H_2O_2$$

All the elements of group I and group II except 'Be' form peroxides. The electronic structure of peroxide ion, O_2^{-2} may be represented as :

$$(:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:)^{2-}$$

6. **Superoxides** : These oxides also contain more oxygen-atoms than required by the elements in the normal oxides. In these oxides the oxidation number of oxygen is – 1/2. The oxide-ion contains one unpaired electron and therefore these oxides are paramagnetic and coloured. The structure of oxide ion in such oxides may be represented as :

$$(:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:\underset{\cdot\cdot}{O}:)^{-}$$

All the metals of group I except Li form super oxides e.g., KO_2. They are oxidizing agents because they give oxygen on treatment with water.

$$4KO_2 + 2H_2O \rightarrow 4KOH + 3O_2$$

7. **Di-oxides :** In these oxides oxidation number of oxygen is -2. For example MnO_2, and PbO_2 (Lead dioxide), they give Chlorine gas with concentrated HCl and oxygen with concentrated H_2SO_4, but do not give H_2O_2.

$$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$$

$$2MnO_2 + 2H_2SO_4 \rightarrow 2MnSO_4 + 2H_2O + O_2$$

8. **Sub-oxides :** They contain less oxygen than required by the element in its normal oxide. They involve M – M as well as M–O bonds but there is no O–O bond.

For example : C_3O_2 (Carbon sub-oxide). N_2O (Nitrous Oxide) and Pb_2O (Lead sub-oxide). The oxidation number of carbon in carbon sub-oxide is $+1\frac{1}{3}$ whereas that of oxygen is the usual -2.

Oxides of the Group VIA Elements:

Elements of Group VIA form a number of oxides. Of all these oxides the dioxides and trioxides are the most important and are discussed in detail.

Di-oxides: MO_2

In this type of oxides the element M shows oxidation state as $+4$. The dioxides of sulphur, Se and Te are described below:

1. **Sulphur Dioxide (SO_2)**

In the laboratory it is prepared by the reduction of concentrated H_2SO_4 with Cu–turnings

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$$

On industrial scale it is prepared by burning sulphur or metal sulphide in air or oxygen.

$$S + O_2 \rightarrow SO_2$$

$$4FeS + 7O_2 \rightarrow 2Fe_2O_3 + 4SO_2$$

Properties :

It is a colourless, poisonous gas with pungent smell. It can be liquefied below $-10^\circ C$ and solidified below $-70^\circ C$. Its density is 32.

Chemical Properties :

1. It is neither combustible, nor supports combustion, but certain metals like Mg, Fe etc, continue to burn in it when heated.

$$2Mg + SO_2 \longrightarrow 2MgO + S$$

$$4K + 3SO_2 \longrightarrow K_2SO_3 + K_2S_2O_3$$

$$3Fe + SO_2 \longrightarrow FeS + 2FeO$$

2. It is highly soluble in water giving H_2SO_3 in solution.

$$SO_2 + H_2O \longrightarrow H_2SO_3 \quad \text{(Sulphurous acid)}$$

Since H_2SO_3 is unstable, SO_2, its acid anhydride is used for the preparation of sulphites. When SO_2 is bubbled through solution of NaOH, Sulphite is produced.

$$SO_2 + 2O\bar{H} \longrightarrow SO_3^{--} + H_2O$$

It excess of SO_2 is passed through the alkali solution, bisulphite is produced.

$$SO_2 + O\bar{H} \longrightarrow HSO_3^-$$

3. Reducing reactions:

In the presence of water it acts as a strong reducing agent and reduces:

(a) Halogens:

$$Cl_2 + 2H_2O + SO_2 \longrightarrow 2HCl + H_2SO_4$$

$$I_2 + 2H_2O + SO_2 \longrightarrow 2HI + H_2SO_4$$

(b) Acidified solution of $KMnO_4$ and $K_2Cr_2O_7$

$$\begin{array}{l} 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O \\ (SO_2 + H_2O + O \longrightarrow H_2SO_4) \times 5 \\ \hline 2KMnO_4 + 2H_2O + 5SO_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4 \end{array}$$

Similarly :

$$\begin{array}{l} K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O \\ (SO_2 + H_2O + O \longrightarrow H_2SO_4) \times 3 \\ \hline K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O \end{array}$$

(c) Ferric salts to ferrous salts

$$2FeCl_3 + SO_2 + 2H_2O \longrightarrow 2FeCl_2 + H_2SO_4 + 2HCl$$

(d) Iodates are reduced with the liberation of Iodine.

$$2KIO_3 + 5SO_2 + 4H_2O \longrightarrow 3KHSO_4 + 3H_2SO_4 + I_2$$

4. **Oxidizing reactions** :

In some of its reactions it acts as an oxidizing agent. For example it oxidizes H_2S to free sulphur and Mg, K etc. to their oxides.

$$2H_2S + SO_2 \longrightarrow H_2O + 3S$$

$$2Mg + SO_2 \longrightarrow 2MgO + S$$

$$4K + 3SO_2 \longrightarrow K_2SO_3 + K_2S_2O_3$$

5. **Bleaching action :**

In the presence of water it acts as a bleaching agent for many vegetable colouring matters. The bleaching action is due to the reduction of the colouring matter by the nascent hydrogen which is produced during reaction.

$$SO_2 + 2H_2O \xrightarrow{\qquad\qquad} H_2SO_4 + 2H$$

Very delicate fibers are also bleached by it. The colour however reappears on exposure, due to the oxidation of the reduced material by air.

6. It combines with chlorine giving sulphuryl chloride :

$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2$$

Uses :

1. Sulphur dioxide has much commercial importance because it is the starting point in the manufacture of sulphuric acid.

2. Liquified sulphur dioxide is used as valuable solvent in the refining of lubricating oils.

3. Its aqueous solution is used as a bleaching agent for straw, wool, silk, sponges and other substances, which are destroyed by chlorine bleaching.

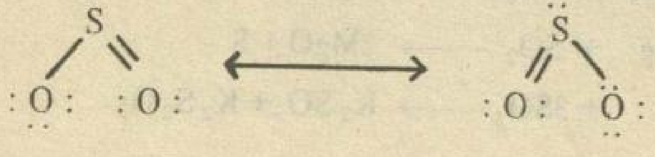
4. It is used as germicide, fungicide and disinfectant.

5. It is used as a refrigerating agent.

Stracture of sulphur dioxide molecule :

The SO_2 molecule has angular or V–shaped structure with a bond-angle equal to 119.5°C.

The electronic structure of SO_2 is a resonanace hybrid of:



Selenium Dioxide SeO_2.

It is prepared by burning Se in air. It is a solid at room temperature and sublimes at 315°C. It is easily reduced to elementary Se and is therefore used as an oxidizing agent. It is soluble in water giving selenious acid (H_2SeO_3) which may be obtained in the crystalline state. The gaseous SeO_2 has the same structure as that of SO_2 but in the solid state it has chain like structure.

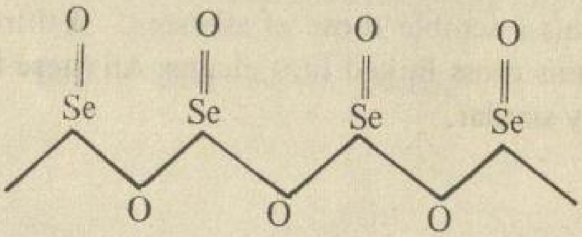


Fig. 8.2

Tellurium Dioxide (TeO_2)

It is also obtained by burning Te in oxygen or air. It is solid which is less volatile than SeO_2 and has ionic rutile structure. It is also used as an oxidizing agent.

TRIOXIDES (XO_3)

All the elements of group VIA form trioxides.

SULPHUR TRIOXIDE (SO_3)

Preparation :

It is prepared by the direct oxidation of sulphur dioxide and oxygen. The reaction is very slow ordinarily but can be accelerated by means of a catalyst such as platinised asbestos or V_2O_5 heated upto 400–450°C.

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

This catalytic oxidation of sulphur dioxide by air is made use of in the contact process for the manufacture of sulphuric acid.

Properties : Physical : At room temperature it is a white solid and exists in three distinct forms. The vapour on cooling first condenses to a liquid form (B.Pt.–44.8). This on standing for a short time solidifies into transparent crystals (M.P.t 16.85 and B.Pt. 44.52°C) with specific gravity 1.9225. This is known as ice form or $\alpha - SO_3$. On further standing at room temperature $\alpha - SO_3$ is converted into $\beta - SO_3$ (m.pt. 32.5). Which is solid whose long silky crystals resemble those of asbestos. A third form is known as γ- SO_3 having chains cross linked into chains. All these forms of sulphur trioxides are chemically similar.

Chemical properties :

1. It reacts with water giving sulphuric acid to obtain fuming sulphuric acid or oleum.

Oleum is then diluted with a calculated quantity of water to get sulphuric acid of any desired strength. The reaction is highly exothermic and SO_3 acts as a strong Lewis acid.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7 \quad \text{(Oleum)}$$

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

2. It is a powerful oxidizing agent, especially when hot. Thus hot SO_3 oxidizes chlorides, bormides and iodides of metals as well as nonmetals to their respective free halogens e.g.

$$2HCl + SO_3 \longrightarrow H_2O + Cl_2 + SO_2$$

$$2HBr + SO_3 \longrightarrow H_2O + Br_2 + SO_2$$

$$2KI + SO_3 \longrightarrow I_2 + K_2O + SO_2$$

It also oxidises C, P and H_2S

$$C + 2SO_3 \longrightarrow CO_2 + 2SO_2$$

$$2P + 5SO_3 \longrightarrow P_2O_5 + 5SO_2$$

$$3H_2S + SO_3 \longrightarrow 3H_2O + 4S$$

3. It combines with basic oxides giving sulphates.

$$BaO + SO_3 \longrightarrow BaSO_4$$

Structure:

SO_3 gas has a plane triangular structure and is a resonance hybrid.

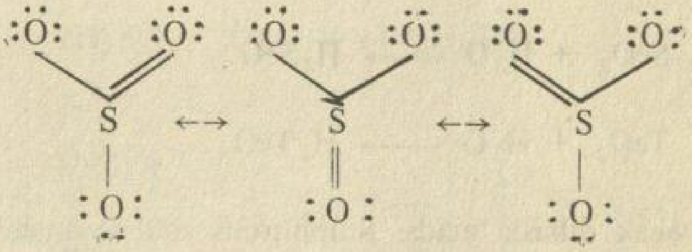


Fig. 8.3

The bond length S – O is 1.45 A° and O – S – O angle of 120° suggest plane triangular system with Sp^2 hybridisation and presence of some dative π-bonding (double Bonding).

OXYACIDS

The elements of group VIA form a large number of oxyacids out of which those of sulphur are numerous and more important. Most of these acids do not exist as free acids, but are known in aqueous solution only and as their salts. S, Se and Te shows various oxidation states in these oxy-acids. The most commonly known oxy-acids are those in which these elements show oxidation state of + 4 and + 6.

1. The oxy acids in which elements show +4 oxidation state are

called Tetravalent oxyacids –H_2XO_3. The name of these acids end in "–ous". while those of their salts in "–ite". For example sulphurous acid and sulphite.

2. The oxyacids in which these elements show oxidation state of +6 are called hexavalent oxyacids –H_2XO_4.

Their names end in "–ic" and the names of their salts end in "–ate." For example sulphuric acid and sulphate.

TETRAVALENT OXYACIDS

These Oxy-acids are generally prepared by the reaction of the dioxides with water. For example :

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$SeO_2 + H_2O \longrightarrow H_2SeO_3$$

$$TeO_2 + H_2O \longrightarrow H_2TeO_3$$

They are weak dibasic acids. Sulphurous acid is unstable and exists in aqueous solution only. It cannot be isolated. Selenious acid (H_2SeO_3) shows similar properties, but it can be isolated in the pure form. H_2TeO_3 resembles H_2SO_3 and cannot be isolated in the pure form.

Sulphurous acid has not been isolated in the free state and like carbonic (H_2CO_3) it exists in aqueous solution only. However, its two series of salts, the sulphites and bi-sulphites are well known. When sulphur dioxide is dissolved in water, H_2SO_3 is formed which ionises in two steps.

$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$$

$$HSO_3^- \rightleftharpoons H^+ + SO_3^{--}$$

The ionization constants at 25°C for the above equilibria are given below.

$$Ka_1 = \frac{[H^+]\,[HSO_3^-]}{[H_2SO_3]} = 1.3 \times 10^{-2} \text{ moles/liter}$$

$$Ka_2 = \frac{[H^+]\,[SO_3^{--}]}{[HSO_3^-]} = 5.6 \times 10^{-8} \text{ moles/liter}$$

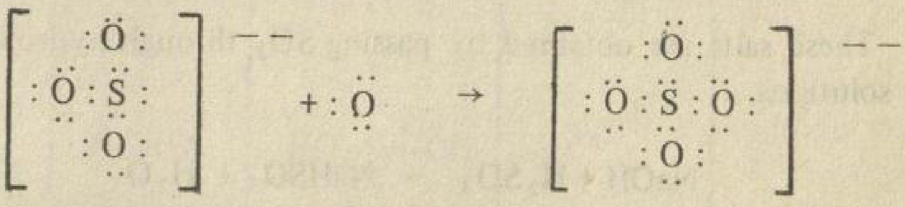
Sulphurous acid is relatively weak acid and not very stable, sulphur dioxide gas is therefore liberated whenever solutions of sulphites are strongly acidified :

$$SO_3^{--} + 2\overset{+}{H} \longrightarrow H_2O + SO_2$$

The H_2SO_3 and its salts are slowly oxidized to sulphate by atmospheric oxygen.

$$2H_2SO_3 + O_2 \longrightarrow 2H_2SO_4$$

OR



(Sulphite ion) (Sulphate ion)

The sulphite ion is also oxidized to sulphate ions by Cl_2. $KMnO_4$, $K_2Cr_2O_7$ and KIO_3. For example.

$$Cl_2 + H_2O + H_2SO_3 \rightarrow H_2SO_4 + 2HCl$$

$$2KMnO_4 + 5H_2SO_3 \rightarrow 2H_2SO_4 + 2MnSO_4 + K_2SO_4 + 3H_2O$$

$$K_2Cr_2O_7 + 3H_2SO_3 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O$$

$$KIO_3 + 3H_2SO_3 \rightarrow 3H_2SO_4 + KI.$$

H_2SO_3 also shows oxidizing character towards strong reducing agents like H_2S and iodide ions.

e.g., $$2H_2S + H_2SO_3 \rightarrow 3S + 3H_2O$$

$$4\overset{-}{I} + \overset{--}{SO_3} + 6\overset{+}{H} \rightarrow S + 2I_2 + 3H_2O$$

The electronic configuration of H_2SO_3 is represented as

$$\begin{array}{c} :\ddot{O}: \\ H:\underset{..}{\ddot{O}}:\underset{..}{S}:\underset{..}{\ddot{O}}:H \text{ or } SO(OH)_2 \end{array}$$

Sulphite and Bisulphites :

We have already seen that sulphurous acid is a diprotic acid and thus gives 2 series of salts–the normal sulphite and bisulphite.

Because of the moderately strong proton affinity of $\overset{--}{SO_3}$ ion, solution of normal sulphite ions are slightly basic. However, since bisulphite ion has a greater tendency to release proton to water rather than to take up, solutions of bisulphites are slightly acidic.

These salts are obtained by passing SO_2 through hydroxide or carbonate solutions.

$$NaOH + H_2SO_3 \rightarrow \underset{\text{(Sod. bisulphite)}}{NaHSO_3} + H_2O$$

$$NaHSO_3 + NaOH \rightarrow \underset{\text{(Sod. sulphite)}}{Na_2SO_3} + H_2O$$

Sulphites and bisulphites of alkali metals are soluble in water, while those of other metals are insoluble. These salts are used as bleaching agents, and food preservatives.

HEXAVALENT OXYACIDS

The hexavalent oxyacids of S, Se and Te in which these elements are in + 6 oxidation state are H_2SO_4, H_2SeO_4, H_2TeO_4. These oxyacids are usually obtained by the reaction of the tri-oxide and water. For example:

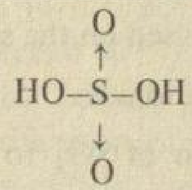
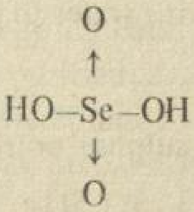
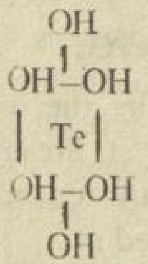
when sulphur tri-oxide is dissolved in water sulphuric acid is produced which ionises in two steps.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

$$H_2SO_4 \rightleftharpoons \overset{+}{H} + HSO_4^-$$

$$HSO_4^- \rightleftharpoons \overset{+}{H} + SO_4^{--}$$

ACIDITY CONSTANTS OF HEXAVALENT OXYACIDS

Acid	Formula	Structure	Ionization Constant	
			Ka_1 mole/litre	Ka_2 mole/litre
Sulphuric acid	H_2SO_4	 $HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-OH$	10^{+9}	10^{-2}
Selenic acid	H_2SeO_4	 $HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{Se}}-OH$	10^{+3}	—
Telluric acid	H_6TeO_6		10^{-7}	—

It may be noted from the above table; that the acid strength decreases down the group. Selenic acid is rather similar in acid strength to sulphuric acid, but is a much stronger oxidizing agent as is shown by the potential for

$$SeO_4^{--} + 4H^+ + 2e^- \longrightarrow H_2SeO_3 + H_2O \qquad E^\circ = 1.15 \text{ volts.}$$

The +6 oxy-acid of Te is quite different from those of S and Se. The formula of Telluric acid is Te $(OH)_6$, and X-Ray crystal structure studies show that the (OH) groups are at the corners of a regular octa-hedron with the Te atom at the centre. Besides the structural difference from H_2SO_4 and H_2SeO_4, Te $(OH)_6$ is a weak dibasic acid with a first ionization constant of about 10^{-7}

Sulphuric acid (H_2SO_4).

Sulphuric acid is commercially the most important acid and is obtained by the oxidation of sulphur dioxide to sulphur trioxide, followed by reaction with water. On industrial scale it is produced by two processes.

1. The lead chamber process.
2. The contact process.

Both of these processes are based on the same principle namely,

(a) Production of sulphur dioxide.
(b) The catalytic oxidation of SO_2 to SO_3 by atmospheric oxygen.
(c) The reaction of SO_3 with water to give sulphuric acid.

Lead Chamber Process:

SO_2 is produced by burning sulphur or iron pyrites.

$$S + O_2 \rightarrow SO_2$$

$$4FeS_2 + 11\,O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

Sulphur dioxide is oxidized by the oxides of Nitrogen NO and NO_2 which act as a homogeneous catalyst. Steam, oxygen from air, sulphur dioxide and oxides of Nitrogen are introduced into lead-lined chambers. The mode of reactions may be represented as :

$$2SO_2 + O_2 + H_2O + NO + NO_2 \rightarrow 2HOSO_2.ONO$$

(Nitrosyl sulphuric acid).

$$2HOSO_2.ONO + H_2O \rightarrow 2H_2SO_4 + NO + NO_2$$

The oxides of Nitrogen are thus regenerated and may be re-used in the process. A coating of lead sulphate is first formed on the lead linings of the chambers which protects the metal from further attack from the acid. The acid produced by this process is relatively dilute and impure. The acid produced by this method needs concentration before it could be used in many industries.

by this method needs concentration before it could be used in many inudstries.

The Contact Process :

This is based upon the reversible combination of SO_2 and O_2

$$2SO_2 + O_2 \rightarrow 2SO_3 ; \qquad \Delta H = 46 \text{ K cals}$$

The reaction is reversible and exothermic. Thus according to Lechatelier principle the favourable conditions for the maximum yield of SO_3 are (1) High pressure and (2) Low temperature.

In practice the process is operated at atmospheric pressure and at a temperature of 450° to $500^\circ C$. The equilibrium is attained in a very short time when the reactants are in contact with a catalyst such as V_2O_5 or Platinised Absestos. The process is shown diagramatically in Fig. (8.4). The sulphur dioxide is obtained by burning sulphur or by roasting Iron pyrite (Sulphide ore) in air. The purification of sulphur dioxide and air, from dust particles, Arsenic and other impurities are very essentail because they might poison the catalyst i.e., destroy its catalytic activity. The sulphur dioxide mixed with an excess of air is purified, dried and then passed through arsenic purifier containing freshly precipitated $Fe(OH)_3$ which absorbs arsenic. The dried and purified gaseous mixture is then passed through a series of converters containing a catalyst. V_2O_5 is the most suitable catalyst for this reaction as it is cheaper and less susceptible to poisoning than platinum. The operating temperature is maintained without external heating by using heat exchangers. After passing through the converters (Contact towers) the gases are cooled and passed through the absorption tower down which concentrated sulphuric acid trickles. SO_3 is absorbed in H_2SO_4 forming oleum or pyrosulphuric ($H_2S_2O_7$). The direct absorption of sulphur trioxide in water is impracticable because the heat evolved causes the solution to boil, producing a fog of fine droplets which are slow to condense. The pyrosulphuric acid obtained from the absorption tower is diluted with a culculated quantity of water.

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7 \quad \text{(Pyrosulphuric acid)}$$

$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4 \quad \text{(Sulphuric acid)}$$

The product marketed from the contact process has a concentration of about 100%. Contact acid is purer than that produced by the chamber process and is therefore preferred for use, such as food processing and drug manufacture. About two third of the world production of sulphuric acid is made by the contact process.

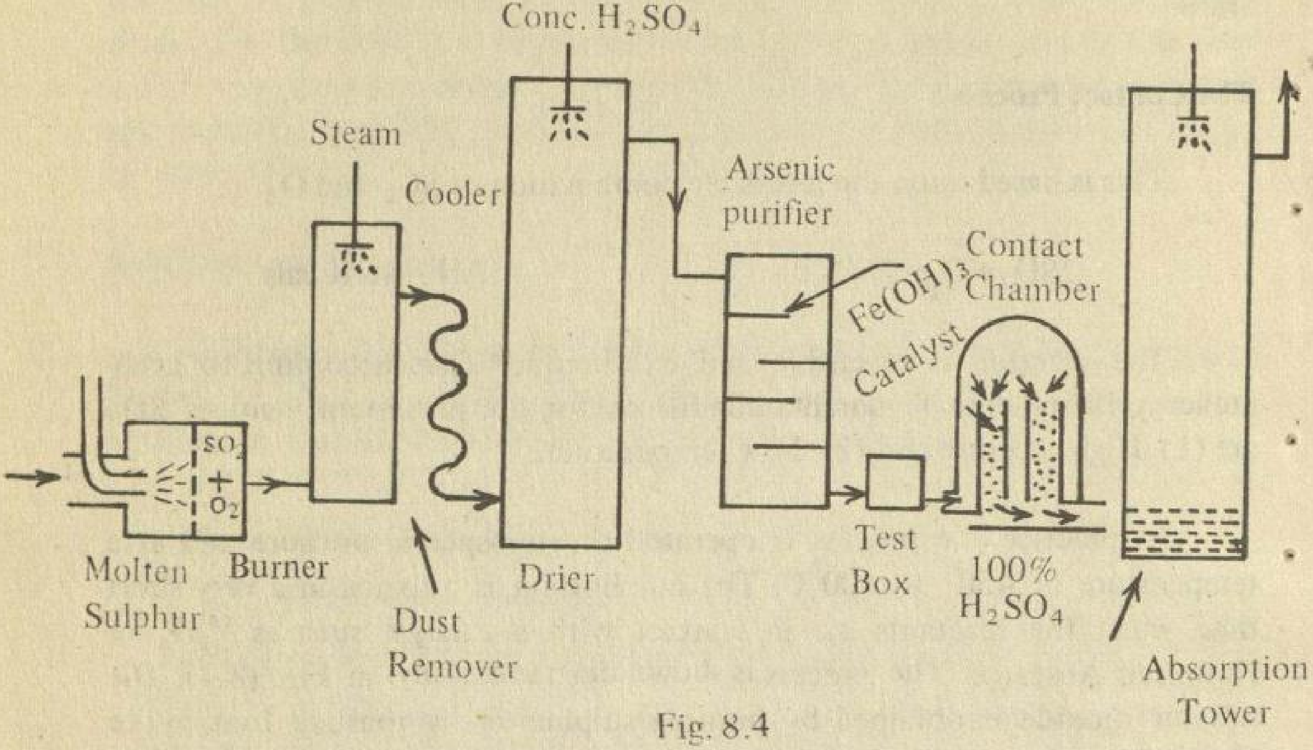

Conc. H_2SO_4
Steam
Cooler
Arsenic purifier
Contact Chamber
$Fe(OH)_3$
Catalyst
SO_2
O_2
Molten Sulphur
Burner
Dust Remover
Drier
Test Box
100% H_2SO_4
Absorption Tower

Fig. 8.4

Properties:

Physical: Concentrated H_2SO_4 (98%) is a thick syrupy liquid that freezes at 10.37°C and boils at 338°C. Pure H_2SO_4 has specific gravity of 1.84 and is miscible with water in all proportions. If a small amount of water is added to concentrated H_2SO_4, sufficient amount of heat is produced which boils the water and thus causes the acid to vigorously spatter out of the container. This is dangerous and care must be taken to add a small quantity of acid to large quantity of water.

Never Add Water to Acid.

Concentrated sulphuric acid is extremely corrosive and should be handled with care; it causes severe burns if brought in contact with the skin. 100% pure H_2SO_4 strongly fumes in air.

Chemical : Chemically sulphuric acid acts both as an acid and as an oxidizing agent.

1. As an acid :

In dilute solution it behaves as a strong dibasic acid. It ionises in two steps.

$$H_2SO_4 + H_2O \rightleftharpoons H_3\overset{+}{O} + HSO_4^-$$

$$HSO_4^- + H_2O \rightleftharpoons H_3\overset{+}{O} + SO_4^{--}$$

The first ionisation is almost complete while the second ionisation occurs to a lesser extent. H_2SO_4 gives two series of salts, bisulphates and sulphates. The bisulphate ion is itself an acid and therefore its solutions are acidic. The solutions of sulphates are neutral. H_2SO_4 neutralizes bases in two steps:

1. $NaOH + H_2SO_4 \rightarrow NaHSO_4 + H_2O$
2. $NaOH + NaHSO_4 \rightarrow Na_2SO_4 + H_2O$

Active metals liberate Hydrogen from dilute sulphuric acid. *e.g.*,

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$
$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$$

Active metals liberate Hydrogen from dilute sulphuric acid. *e.g.*,

2. As an oxidizing agent :

Hot concentrated H_2SO_4 oxidizes both metals and non-metals forming sulphates and liberating sulphur dioxide gas. For example :

(i) $Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$

(ii) $Zn + 2H_2SO_4 \rightarrow ZnSO_4 + SO_2 + 2H_2O$

(iii) $C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$

It oxidizes bromides liberating bromine.

$$2H^+ + 2\bar{Br} + H_2SO_4 \rightarrow Br_2 + 2H_2O + SO_2$$

Powerful reducing agents such as HI will reduce H_2SO_4 to H_2S and S.

$$2H^+ + 2\bar{I} + H_2SO_4 \rightarrow I_2 + 2H_2O + SO_2$$

Sulphur and carbon are oxidized to the corresponding oxides.

$$C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$$

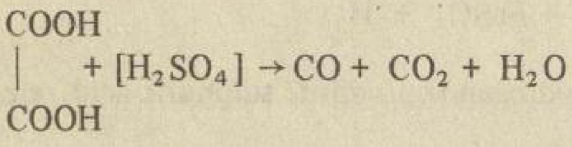
$$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$$

3. **As dehydrating agent:**

Concentrated H_2SO_4 is a powerful dehydrating agent or disiccant. It removes water molecules from a large number of compounds *e.g.*,

$$\underset{\text{(Sugar)}}{C_{12}H_{22}O_{11}} \xrightarrow{\text{conc. } H_2SO_4} 12C + 11H_2O$$

$$\underset{\text{(Formic acid)}}{HCOOH} \xrightarrow{\text{conc. } H_2SO_4} CO + H_2O$$



$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} + [H_2SO_4] \rightarrow CO + CO_2 + H_2O$$

(oxalic acid)

$$\underset{\text{(ethyl alcohol)}}{2C_2H_5OH} \longrightarrow C_2H_5OC_2H_5 \text{ (diethyl ether)} + H_2O$$

The charring of sugar, paper, cotton and wood etc, by concentrated H_2SO_4 is due to its dehydrating property.

4. **As a sulphonating agent :**

Most of the aromatic hydrocarbons, such as Benzene, when treated with 100% H_2SO_4 give sulphonic acid.

Thiosulphates : These are sulphates in which an oxygen atom is being replaced by sulphur atom giving the ion $S_2O_3^{--}$. Sodium thiosulphate, commonly known as hypo, is the most important thio-salt. It is prepared by boiling a solution of sodium sulphite with sulphur for sufficient time. If the excess of sulphur is filtered off and the filtrate is concentrated, colourless crystals of the penta hydrate, $Na_2S_2O_3 . 5H_2O$ appear on cooling.

It melts as 48°C. The thiosulphate is decomposed by dilute acids giving SO_2 and slowly depositing S as a yellow precipitate.

$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2 \uparrow + S \downarrow$$

With iodine, sodium thiosulphate forms sodium tetrathionate.

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

This reaction which is rapid even at room temperature is used in volumetric estimation of iodine in solution. Sodium thiosulphate solution is used in photography to fix the negative. This it does by forming a soluble complex ion of the type:

$$2AgBr + S_2O_3^{--} \rightarrow [Ag_2(S_2O_3)]^{-} + Br^{-}$$

It is used as an anticolor to remove any residual chlorine from the fabric after bleaching.

$$Na_2S_2O_3 + 4Cl_2 + 5H_2O \rightarrow Na_2SO_4 + 8HCl + H_2SO_4$$

QUESTIONS

1. Compare the physical properties of elements of group VIA.
2. What is allotropy? Discuss briefly the allotropic modifications of oxygen and sulphur.
3. Write the electronic formula and suggest the geometry of the following:

$$SO_2, SO_3, SO_4^{--}, S_2O_3^{--}, H_2S, S_2Cl_2, S_2Cl_4, SF_6,$$

4. Complete and balance the following equations:

   KNO_3 + heat →

   $Na_2O_2 + H_2O$ →

   Na_2S + HCl →

   Cu + Conc. H_2SO_4 + heat →

   C + Conc. H_2SO_4 + heat →

   $FeS_2 + O_2$ + heat →

   $Na_2S_2O_3 + I_2$ →

5. Compare and contrast the properties of H_2S and H_2O. Why at ordinary temperature water is in the liquid state while H_2S is a gas.

6. How could you show that (i) H_2S is an acid; (ii) is a reducing agent; (iii) contains sulphur?

7. Sulphur dioxide acts both as an oxidizing agent and reducing agent but H_2S acts only as a reducing agent. Explain and give equations to illustrate your answer.

8. Classify oxides according to their chemical behaviour and constitution. Give two examples of each class with illustrative reactions and equations.

9. How is sulphuric acid prepared on industrial scale.

   Show that sulphuric acid is:

   (1) A dibasic acid. (2) Oxidizing agent (3) Dehydrating agent. (4) Sulphonating agent.

10. Explain the following statements.

    (i) It is incorrect to refer to conc. H_2SO_4 as strong acid.

    (ii) On dissolving in water HCl ionizes but KCl only dissociates.

(iii) Oxygen shows different behaviour from the rest of the elements of group VI.

11. Write equations for the reactions by which the following conversions could be accomplished in the lab:

$$SO_3 \rightarrow CaSO_4$$

$$Na_2SO_3 \rightarrow Na_2S_2O_3$$

$$BaCl_2 \rightarrow BaSO_4$$

$$ZnCO_3 \rightarrow ZnSO_4$$

$$\overset{+}{NH_4} \rightarrow (NH_4)_2SO_4$$

12. Show:-

(i) In what compound oxygen has oxidation state of +2.

(ii) What reactions take place when sulphur dioxide is bubbled through aqueous solutions of the following substances:

(a) Cl_2 (b) $NaHCO_3$ (c) NH_3 (d) $Ba(OH)_2$ (e) H_2S.

(iii) What volume of sulphur dioxide at 25°C and I atmosphere is produced when copper reacts with 14 grams of conc. H_2SO_4.

13. Describe the contact process for the production of sulphuric acid. Give its reaction with (a) Carbon (b) Sulphur. (c) Marble. (d) Cane sugar. (e) Benzene. (f) Copper. (g) Zinc. (h) Hydroiodic acid.

CHAPTER 9

GROUP VII A ELEMENTS

THE HALOGENS

Elements Fluorine, Chlorine, Bromine, Iodine and Astatine, are collectively known as halogens or salt producing elements. These elements show close similarities in properties and thus form a separate family in the periodic table. They are very reactive and highly electronegative elements. They form negative halide ions in their ionic compounds. Except Fluorine, all other halogens also show positive oxidation states. Astatine is a short lived radio-active element and thus occurs rarely in nature. The electronic configurations of these elements are given in the following table :

Table. 8·1

Name of Element	Symbol	At. No.	At. Wt.	Electronic Configuration
Fluorine	F	9	18.998	$[\mathrm{He}]\ 2S^2\ 2P^5$
Chlorine	Cl	17	35.453	$[\mathrm{Ne}]\ 3S^2\ 3P^5$
Bromine	Br	35	79.909	$[\mathrm{Ar}]\ 3d^{10}\,4S^2\,4P^5$
Iodine	I	53	126.904	$[\mathrm{Kr}]\ 4d^{10}\,5S^2\,5P^5$
Astatine	At	85	210.00	$[\mathrm{Xe}]\ 4f^{14}\,5d^{10}\,6S^2\,6P^5$

As shown in the above table each element has outer $S^2 P^5$ electronic configuration *i.e.*, seven electrons in the valence shell. Hence they are placed in the 7th group of the periodic table. The arrangement of electrons in the valence shell reveals that each element has one unpaired electron in one of the p-orbitals. Thus they either gain an electron by forming an ionic bond giving X-ion or form a covalent bond in order to complete their octet. In most of their common compounds halogens show oxidation state of -1. Fluorine, being the most electronegative element, is always in the oxidation state of -1, but among other halogens oxidation states of $+1, +3, +5, +7$, are possible. The higher oxidation states arise by the use of d-orbitals and are generally found in the inter-halogen compounds and halogen oxides. For example the oxidation state of chlorine in Cl_2O_7 is $+7$, while the oxidation states of Cl, Br and I, in $Cl\,F_3$, $Br\,F_5$ and $I\,F_7$ are $+3$, $+5$ and $+7$ respectively. Because of their higher electronegativities, the halogens show almost no metallic properties, though solid Iodine has a somewhat metallic appearance. The similarities and gradations in the properties of halogens are shown in the following table:

Halogen	M.Pt. K°	B.Pt. K°	Density g/cm^3	Atomic Radius A°	Ionic Radius A°	I.P (e.v)	Electron affinity (e.v.)	Bond energy K Cal/mole	Electronegativity
F(9)	55°	85°	1.11	0.72	1.36	17.4	3.62	37	4.0
Cl(17)	172°	338.9°	1.56	0.99	1.81	13.0	3.79	58	3.0
Br(35)	265°	381.8°	3.12	1.14	1.95	11.8	3.56	46	2.8
I(53)	387°	457°	4.93	1.33	2.16	10.4	3.28	36	2.5

From the above table the following general trend in the properties of Halogens can be observed :

Small amounts of Fluorine are also found in the combined state in bones, and sea water. Deposits of Fluorspar are found in Pakistan in Kalat, Chitral and Gilgit.

2. **Chlorine**: In the combined state it occurs:

(i) as Chloride ion Cl^-, in Sea water (2%).

(ii) In rock salt beds of the mineral halite and NaCl.

(iii) In salt beds of KCl, $MgCl_2$ and $CaCl_2$.

(iv) In the human gastric juices as HCl (0.03%).

In Pakistan rock salt deposits are found in Kohat district (N.W.F.P.) and Khewra (Punjab).

3. **Bromine**: It occurs as bromides of Na, K. and Mg in sea water.

4. **Iodine**: It occurs;

(i) As iodine ion, I^-, in sea water (.000004%)

(ii) As sodium iodate ($NaIO_3$) in Chile saltpeter ($NaNO_3$)

(iii) In sea weed such as Kelp.

Preparation:

Fluorine: Because no chemical oxidizing agent can remove electron from the F^- ion, electrolytic methods are used to prepare fluorine. It is usually prepared by the electrolysis of fused K F and H F or Potassium hydrogen fluoride (KHF_2). The electrolysis is carried out in a V – shaped vessel made of Ni, Cu and Fe alloy having Ni or graphite electrodes. The temperature of the electrolyte is kept around 250°C. On electrolysis the Fluorine formed first reacts with Nickle, copper and Iron of the container forming a thin coating of Fluorides which is very resistant to further attack. Fluorine is collected at the anode and hydrogen gas at the cathode.

$$\begin{array}{lcl} 2KF \rightarrow 2K^+ & & +2F^- \\ \qquad\quad\ \downarrow & & \ \ \downarrow \\ 2K + 2HF = 2KF + H_2 & & F_2 \text{ (anode)} \\ \qquad\quad \text{(cathode)} & & \end{array}$$

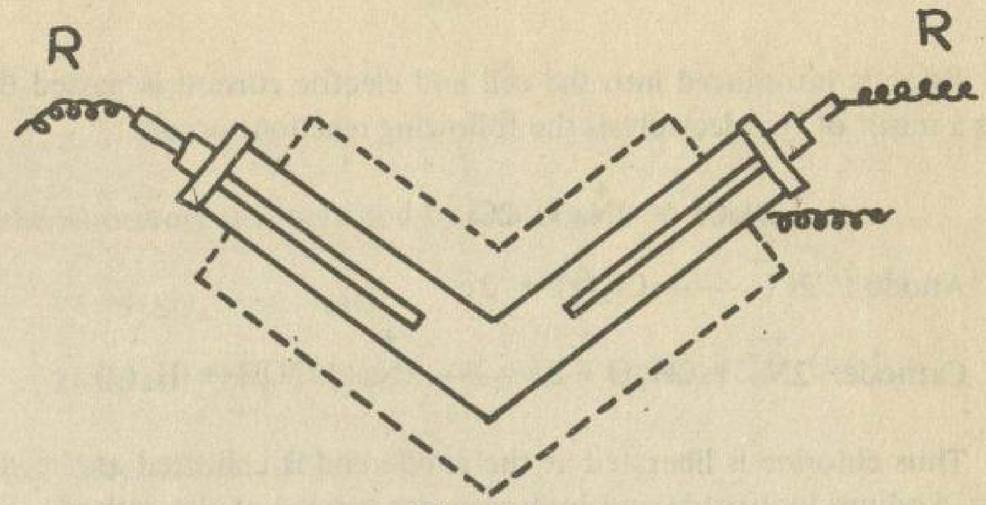


Fig. 9.1

Chlorine: Chlorine is usually prepared in the laboratory by the oxidation of conc. HCl by oxidizing agents:

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$
$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

Instead of HCl a mixture of NaCl and Conc. H_2SO_4 may be used in the preparation of Cl_2 by the above method.

Caution : Always prepare Cl_2 in a fume chamber because it is poisonous.

Commercial preparation of Chlorine:

On industrial scale chlorine is prepared by the electrolysis of a concentrated solution of sodium chloride (Brine). One type of cell used is the Nelson cell. It consists of a U-shaped perforated steel vessel which acts as a cathode. The cathode is coated inside with a porous diaphragm of compressed asbestos which separtes the cathode from the anode. The U-shaped vessel is supported in a steel tank having an outlet for hydrogen gas. The carbon rod acts as anode and is suspended in the U-Tube Fig. (9.2).

Brine is introduced into the cell and electric current is passed through it. As a result of the electrolysis the following reactions occur:

$$2NaCl \rightleftharpoons 2\overset{+}{Na} + 2\overset{-}{Cl}$$

$$\text{Anode}: \; 2\overset{-}{Cl} \longrightarrow Cl_2(g) + 2\overset{-}{e}$$

$$\text{Cathode}: \; 2\overset{+}{Na} + 2H_2O + 2\overset{-}{e} \longrightarrow 2\overset{+}{Na} + 2\overset{-}{OH} + H_2(g)$$

Thus chlorine is liberated at the anode and is collected at the chlorine outlet. Sodium hydroxide and hydrogen are formed at the cathode. Sodium hydroxide is collected in the catch basin placed under the U-tube while hydrogen gas is collected at the hydrogen outlet. In this process sodium hydroxide, hydrogen and chlorine are prepared simultaneously.

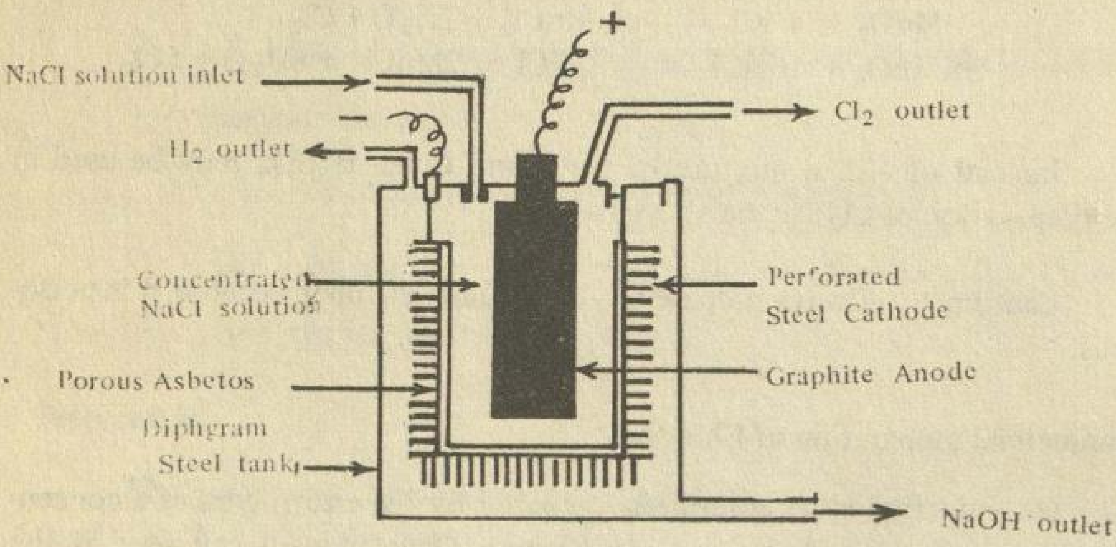

+
NaCl solution inlet
−
H_2 outlet
Cl_2 outlet
Concentrated NaCl solution
Perforated Steel Cathode
Porous Asbetos Diphgram
Graphite Anode
Steel tank
NaOH outlet

Fig. 9.2

Bromine:

Sea water is the principal source of bromine. It is treated with chlorine to release free bromine from the bromides.

$$Cl_2 + 2\overset{-}{Br} \longrightarrow 2\overset{-}{Cl} + Br_2(g).$$

Iodine:

In the laboratory it is prepared by heating a mixture of

KI, H_2SO_4 and MnO_2

$$2KI + 2H_2SO_4 + MnO_2 \rightarrow K_2SO_4 + MnSO_4 + 2H_2O + I_2$$

Commercial preparation of Iodine:

The chief source of iodine from which it is economically obtained is Chile saltpeter ($NaNO_3$) which contains iodine as sodium iodate (**$NaIO_3$**). The chile saltpeter is dissolved in water and the solution is heated till the crystalization of $NaNO_3$ sets in. After the crystalization the mother Liquor, which is left behind, is taken and heated with $NaHSO_3$ which reduces $NaIO_3$ to free iodine.

$$5NaHSO_3 + 2NaIO_3 \rightarrow 2Na_2SO_4 + 3NaHSO_4 + H_2O + I_2$$

Properties of Halogens:

1. **Physical Properties:**

At room temperature fluorine is a pale-yellow diatomic gas; chlorine is a greenish-yellow diatomic gas; Bromine is reddish brown liquid and Iodine is in the form of violet grey crystals. They are almost all soluble in water to varying extent. The solubility decreases down the group as the atomic number is increased. Fluorine is readily soluble in water. Chlorine and Bromine dissolve to a comparatively lesser extent, while iodine is sparingly soluble. Iodine can however be dissolved by mixing it with a small quantity of potassium iodide in solution. The solubility of iodine in KI solution is due to the formation of soluble I_3^- Ions. Some of the physical properties have already been summarized earlier.

Chemical Properties :

Halogens are very reactive and have very high electron affinities. The halogens acts as strong oxidizing agents because all of them gain electrons when reacted with other elements. They are reduced to halides in a chemical reaction. The reduction potentials of halogens are given below :

$F_2 + 2\bar{e} \rightarrow 2F^-$: $E^\circ = 2.87$ volts

$Cl_2 + 2\bar{e} \rightarrow 2Cl^-$: $E^\circ = 1.36$ volts

$Br_2 + 2\bar{e} \rightarrow 2Br^-$: $E^\circ = 1.07$ volts

$I_2 + 2\bar{e} \rightarrow 2I^-$: $E^\circ = 0.54$ volts

Thus Fluorine is the strongest oxidizing agent and the oxidizing power decrease down the group as the atomic number is increased. For the same reasons the fluoride ions act as weaker reducing agents and the reducing power increases down the group.

Halogens oxidize metals, non-metals and many other substances forming halides.

1. **Combination with metals :**

When heated with metals they form halides.

$2Na + Cl_2 \longrightarrow 2NaCl$

$Cu + Br_2 \longrightarrow CuBr_2$

$2K + I_2 \longrightarrow 2KI$

Fluorine reacts vigorously.

2. **Combination with non-metals:**

They oxidize non-metals when heated, forming the corresponding halides.

$2P + 3Cl_2 \rightarrow 2PCl_3$; $2P + 5Cl_2 \rightarrow 2PCl_5$

$2P + 3Br_2 \rightarrow 2PBr_3$; $2P + 5Br_2 \rightarrow 2PBr_5$ (unstable)

$2P + 3I_2 \rightarrow 2PI_3$; $2P + 5I_2 \rightarrow 2PI_5$ (unstable)

3. Combination with some covalent compounds:

They combine with most of the covalent compounds giving halides. For example :

$$PCl_3 + Cl_2 \rightarrow PCl_5$$

$$CO + Cl_2 \rightarrow COCl_2 \text{ (Carbonyl chloride)}$$

$$SO_2 + Cl_2 \rightarrow SO_2Cl_2 \text{ (Sulphuryl chloride)}$$

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2 \text{ (Ethylene Dichloride)}$$

4. Displacement of other Halogens :

Fluorine is an extremely strong oxidizing agent and it replaces chlorine from chloride solutions. Similarly chlorine will displace bromine from bromide solution. In general a halogen of greater oxidizing power will oxidize halide ions of halogen with lower oxidizing power and thus displace it. For example :

$$Cl_2 + 2KBr \longrightarrow 2KCl + Br_2$$

$$Br_2 + 2KI \longrightarrow 2KBr + I_2$$

5. Action with water :

Fluorine reacts violently with water giving hydrogen fluoride along with atomic oxygen.

$$F_2 + H_2O \rightleftharpoons 5HF + O$$

Chlorine and bromine reacts slowly with water in a reversible reaction.

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl \text{ (hypochlorous acid)}$$

$$Br_2 + H_2O \rightleftharpoons HBr + HOBr \text{ (hypobromous acid)}$$

6. Reaction with Organic compounds:

Chlorine and bromine react with hydro-carbons forming halogenated products. The degree of halogenation may often be controlled : e.g.

$$C_6H_6 + Br_2 \longrightarrow C_6H_5Br + HBr$$

$$C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$$

Chlorine reacts with Methane giving the following series of reactions:

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

$$CH_3Cl \longrightarrow CH_2Cl_2 \longrightarrow CHCl_3 \longrightarrow CCl_4$$

(with chlorine)

Uses of Halogens:

Fluorine is so reactive that its commercial uses are limited. Fluorides are added to drinking water to check tooth decay. Organo fluorine compounds are resistant to heat, acids and oxidizing agents. They have found wide use in industry. One such compound is TEFLON which is used as a coating for cooking utensils.

Chlorine is used for bleaching, disinfection of water supplies. $KClO_3$ is used as an oxidizing agent in matches and fire works. Bromine is used as silver bromide in photographic emulish. Deficiency of iodine in human diet may cause the disease of goitre.

Compounds of Halogens:

Halogens combine with almost all the metals and non-metals. Some important compounds of halogens are given below :

Hydrogen Halides :

The hydrogen halides can be prepared by the direct combination of hydrogen and the halogens.

$$H_2 + X_2 \longrightarrow 2HX$$

The heat of formation decreases from HF to HI.

Hydrogen fluoride and hydrogen chloride are also made by the action of concentrated sulphuric acid on the halide salts :

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF(g)$$

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl(g)$$

However, HBr and HI, cannot be made by this reaction, because sulphuric acid being a strong oxidizing agent, will produce Br_2 and I_2 from Br^- and I^-, respectively. For this reason phosphoric acid (H_3PO_4) and halide salts are used for the preparation of HBr and HI;

$$NaBr + H_3PO_4 \longrightarrow HBr(g) + NaH_2PO_4$$

$$NaI + H_3PO_4 \longrightarrow HI(g) + NaH_2PO_4$$

Solutions of hydrogen halides in water are known as hydrohalic acids.

$$HX + H_2O \longrightarrow H_3O^+ + X^-$$

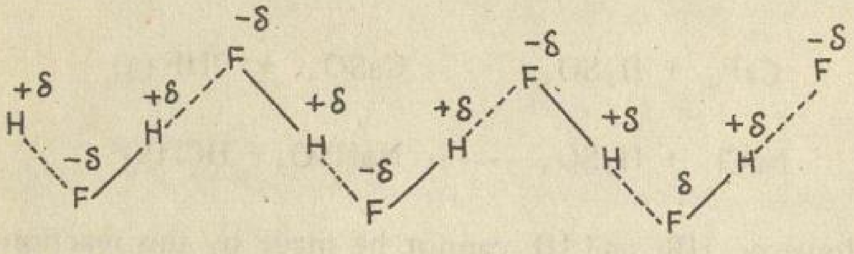
$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$
(Hydrochloric acid)

The HF remains almost unionized in water while the HCl, HBr and HI are highly ionized in solution.

Some physical properties of the hydrogen halides are given in the Table below:

HX	M.P°C	B.P°C	Boiling Point of Acid Solution Constant Boiling Mix.	%Ionization in $\frac{M}{10}$ Solution at 18°C
HF	–92.3	19.4	120	10
HCl	–114	–85	110	92
HBr	–88.5	–67	126	92
HI	–50.8	–35.4	127	92

The high values of the M.P. and the B.P. of the HF and its low degrees of ionization can be explained on the basis of association of HF molecules through hydrogen bonding.



Oxyhalogen Acids :

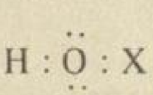
Only chlorine, bromine and iodine form oxyacids because they can exist in positive oxidation state when combined with oxygen.

This is so because oxygen is more electronegative than these halogens. The acids containing both oxygen and halogens are known as oxyhalogen acids. The known oxyacids are listed in the Table below:

Oxyhalogen Acids

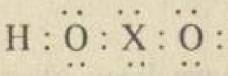
Formula of Acid	Name of acid	Name of the acid anion
$HClO$, $HBrO$, HIO	hypohalous acid	hypohalite ion
$HClO_2$ – –	halous acid	halite ion
$HClO_3$ $HBrO_3$ HIO_3	halic acid	halate ion
$HClO_4$ $HBrO_4$ HIO_4	perhalic acid	perhalate ion

The general structure of the oxyhalogen acids and the oxidation number of the halogen are :



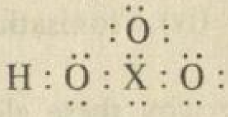
$\mathrm{H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:X}$

(+1)



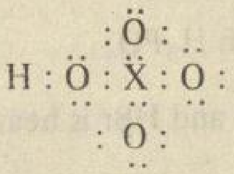
$\mathrm{H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:}$

(+3)



$\mathrm{H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\overset{:\overset{\cdot\cdot}{O}:}{\underset{\cdot\cdot}{X}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:}$

(+5)



$\mathrm{H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\overset{:\overset{\cdot\cdot}{O}:}{\underset{:\underset{\cdot\cdot}{O}:}{X}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:}$

(+7)

The acidity and oxidizing power of the oxyhalogen acids increase in **the order** $HXO < HXO_2 < HXO_3 < HXO_4$. When compounds of the same oxidation number are compared, oxychlorine acids are stronger oxidizing agents and stronger acids than the oxybromine acids, which is turn are stronger oxidizing agents than the oxy iodine acids.

The increasing oxidizing power of oxyhalogen acids from $HXO < HXO_2 < HXO_3 < HXO_4$ is due to increasing number of oxygen atoms in the acid molecules. The increasing acidity with the increase in the oxidation state of the halogen is also attributed to the effect of added oxygen atoms on the strength of the O–H bond with respect to dissociation. The addition of oxygen atoms tends to remove electron away from the less electronegative halogen atom which tends to pull electrons away from the O–H bond. As a result of decreased electron density near the hydrogen in the O–H bond, its dissociation as a proton is greatly facilitated.

QUESTIONS

1. Compare the elements of the group VIIA (Halogens) in respect of their :

   (i) Electronic configuration.

CHAPTER 10

TRANSITION ELEMENTS

Transition elements are those elements, the atoms or ions of which contain partially filled d or f orbitals. This group includes the elements from Scandium (Z = 21) to copper (29), yttrium (39) to silver (47) and Lanthanum (57) to gold (79). A fourth transition series starts with actinium (89), but is not yet complete. The elements which have only 'd' orbitals incomplete are called as "d" block elements or outer-transition elements; on the other hand the elements which have an incomplete 'f' as well as an incomplete 'd' orbitals are called "f" block or inner-transition elements. These include the elements from cerium (58) to lutetium (71) the 4f or more commonly the Lanthanides and the elements from thorium (90) to lawrencium (103), the 5f or more commonly, the Actinides.

General Properties :

In this chapter we shall discuss the chemistry of d-block elements. The d-block elements or outer transition elements, because of the presence of electrons in outer 'd' orbitals, show close similarity in their properties. The first-row transition elements are of greatest importance since they are most abundant.

1. ELECTRONIC CONFIGURATION

In Table 10.1 are given the detailed electronic configuration of the first row transition elements. The building up of electronic configuration of atoms is seen to follow a simple and regular pattern for the first twenty elements, and then to exhibit somewhat more erratic behaviour. The 3s and 3p levels are complete at magnesium (12) and Argon (18), respecttively. The energy of 3d level is generally somewhat higher than that of the 4s sub-level and therefore the latter is filled first, being completed at calcium. In the succeeding ten elements (from Sc to Zn) the 3d level is filled but not perfectly regularly because the 3d and 4s shells do not differ greatly in energy. In case of Cr (24) the electronic configuration is $4s^1$, $3d^5$ instead of $4s^2$ $3d^4$ because of greater stability of half-filled 3d subshell. The electronic configuration of Cu is $3d^{10}$ $4s^1$ and not $3d^9$ $4s^2$. This is because the completely filled 3d subshell gives extra stability. Zinc, however, is not a transition element as it does not have partially filled d orbital in any oxidation state.

Table 10.1

Electronic Configuration of first Transition Series

Sc	21	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^1, 4s^2$
Ti	22	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^2, 4s^2$
V	23	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^3, 4s^2$
Cr	24	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$
Mn	25	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^2$
Fe	26	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^2$
Co	27	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^7, 4s^2$
Ni	28	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^8, 4s^2$
Cu	29	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$

2. METALLIC CHARACTER

All the transition elements are metals. As a group, these elements are characterized by high densities, low atomic volume, high melting points, high boiling points and abilities to form alloys both with each other and with some of the representative elements. Within any particular transition series there is a well defined similarity among the members (Table 10.2). Such similarities, of course are due to the electronic arrangements and sizes. There are only 2 electrons in the outermost shell and the atomic size is smaller than that of the elements of Group IA and Group IIA.

Table 10.2

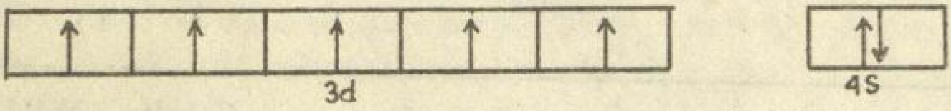
Numerical Properties of Elements of some of the first Transition Series:

Properties	Chromium (Cr)	Manganese (Mn)	Iron (Fe)	Cobalt (Co)	Nickle (Ni)
Atomic Weight	52.01	54.49	55.83	58.94	58.69
Density (20°C)	7.1	7.4	7.9	8.7	8.98 g/cc
Atomic Volume	7.3	7.5	7.0	6.8	6.6
Specific Heat (0°C)	0.104	0.107	0.105	0.099	0.106
Atomic Number	24	25	26	27	28
Electrode Potential (25°C)	–0.74 (Cr^{+3})	–1.18 (Mn^{+2})	–0.44 (Fe^{+2})	–0.28 (Co^{+2})	–0.23 (Ni^{+2})
First Ionization Potential	6.76	7.53	7.9	7.86	7.63ev
Heat of Formation of Oxide	–	–91 (MnO)	–64 (FeO)	–64 (CoO)	–59.7 (NiO)
Melting Point °C	1,800	1,260	1,535	1,492	1,453
Boiling Point °C	2,300	2,150	2,800	3100	2,800

3. OXIDATION STATES

Perhaps the most striking property shown by the transition elements is that they exhibit several oxidation states or show variable valency. The knowledge of the electronic structure of the atoms concerned helps very much in the understanding of this strange behaviour. For example, consider the electronic structure of an atom of manganese. Shell 3 (the M shell) is capable of containing a maximum of eighteen electrons : $S^2P^6d^{10}$. This shell for manganese has five d electrons deficient. The d^5 electrons in Manganese are distributed singly according to the Hund's Rule of maximum multiplicity.

If the electrons of Mn are pictured as follows.



it will be seen that the manganese atom possesses, besides the two normal valency S electrons in the fourth shell, five unpaired electrons in the third shell. This structure accounts in large measure for the variable oxidation states of manganese from + 1 up to the maximum of + 7. Thus in general the several oxidation states of transition elements are possible due to use of S electrons in chemical bonding. The maximum oxidation state is limited by the total number of 4S and 3d electrons present in the first transition series. Known oxidation states for the various metals of the first transition series are summarised in Table 10.3 given below.

Table 10.3

Oxidation states of the first transition series:

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
	+ 2	+ 2	+ 2	+ 2	+ 2	+ 2	+ 2	+ 1
+ 3	+ 3	+ 3	+ 3	+ 3	+ 3	+ 3	+ 3	+ 2
	+ 4	+ 4		+ 4		+ 4		
		+ 5	+ 6	+ 6	+ 6			
				+ 7				

The decrease in the number of higher oxidation states beyond manganese is due to the increase in ionization energy with atomic number. Besides the important property of variable valency, the unfilled d sub-shell of electrons in the atoms of transition element is undoubtedly the cause of several other unique properties of these elements. Such properties include, the furnishing of coloured ions, the ready formation of complex ions, the ready formation of interstitial compounds, catalytic power and special magnetic properties.

4. COLOUR

The phenomenon of colour is related to the absorption of certain wavelengths of white light by the atoms or ions in solution to promote electrons to levels of higher energy. The colour we see is the complement of that absorbed by the electron. For example, if the colour of a cupric compound appears to be blue, that means that colour from yellow orange part of the spectrum of white light is being absorbed. In transition elements compounds there are vacant d orbitals which are higher in energy than the ground state energy levels. It is the transition of electrons between these levels which accounts for the visible spectra of these ions. The colour of the compounds of transition elements is thus attributed to the presence of d electrons and partially filled d sub-shell in their structure.

5. COMPLEX ION FORMATION

The transition metals have a marked tendency to form complex ions. The complex ion consists of a central metal cation to which anions or molecules are attached in a definite geometry with respect to the centre. The anions or molecules are called Ligands and have one or more electron pairs that can be used in bonding to the metal ion. The number of groups of atoms bonded to the metal ion is known as the *Coordination number* of the ion. For example, $[Cu(NH_3)_4]^{+2}$ is a complex ion with the central Cu^{+2} ion, NH_3 molecules as ligands and the coordination number of Cu^{+2} is 4. This tetramine copper (II) complex ion is blue in colour.

Complexes with coordination number two to nine are known, but the 4 and 6 coordinated ones are more common, *e.g.*, $[Ni(CN)_4]^{-2}$ and $[Fe(CN)_6]^{-3}$.

Six coordinated complexes have octahedral geometry, *i.e.*, the 6 ligands are located at the corners of a regular octahedron (Fig. 10.1).

Examples, $[Fe(CN)_6]^{-3}$. $[Co(NH_3)_6]^{+3}$, $[Cr(NH_3)_6]^{+3}$, $[FeF_6]^{-3}$

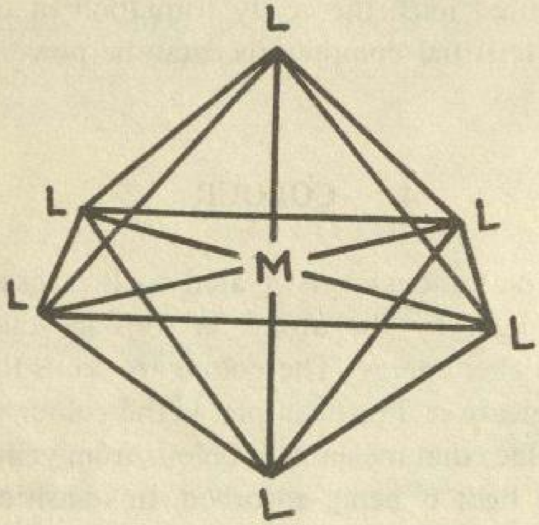


Fig. 10.1

Four coordinate complexes may be either square planar or tetrahedral, as shown in Fig. 10.2.

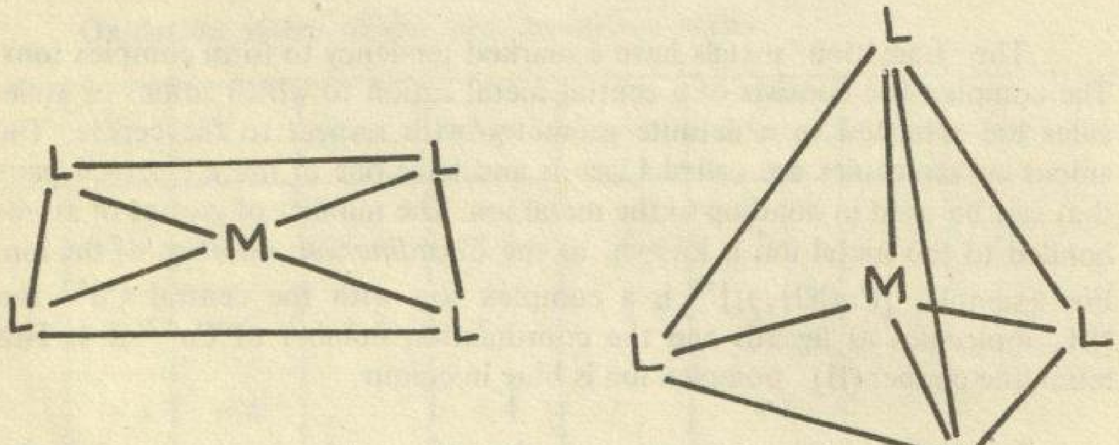
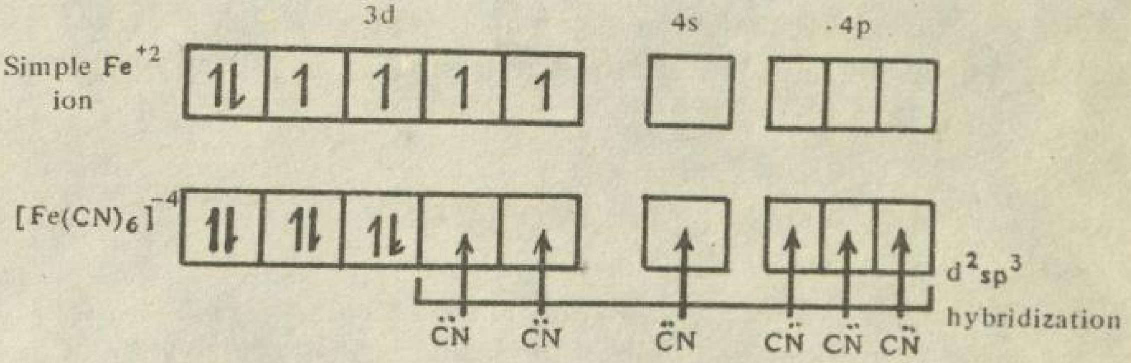


Fig. 10.2

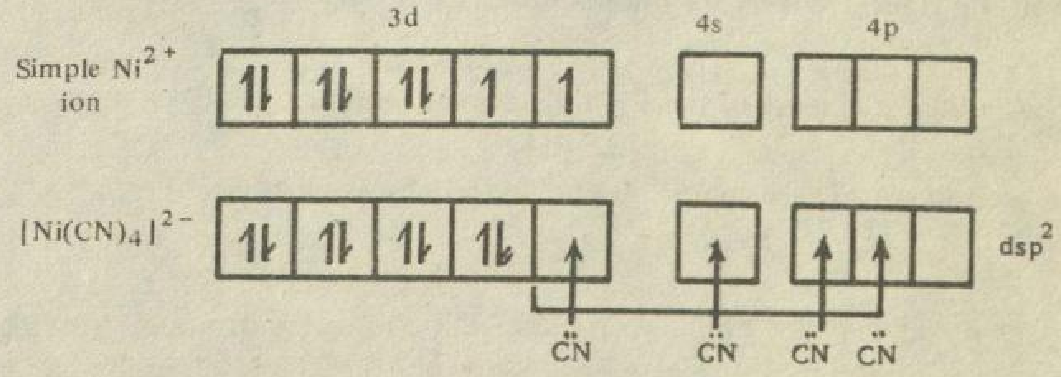
For example, $[Cu(NH_3)_4]^{+2}$, $[Ni(CN)_4]^{-2}$, $[Pd\ Cl_4]^{-2}$ are square planer while $[Co\ Cl_4]^{-2}$ and $[Ni(CO)_4]$ are tetrahedral in structure.

The nature of chemical bond in complex ion can be explained in terms of the *Valency Bond Theory*. According to this theory the central metal ion has a number of unfilled or partially filled d, s and p orbitals. These orbitals hybridize or combine to produce hybrid orbitals of equal energy and are directed in space. For example d^2sp^3 hybridization (two d, one s and 3p orbitals combine to produce six equivalent orbitals directed to the six corners of a regular octahedron. In a square planer complex dsp^2 hybridization takes place while sp^3 hybridization of metal ion orbital gives tetrahedral geometry. The vacant hybrid orbitals of metal atom overlap with the orbitals of the ligands to form polar covalent bonds.

Electronic Structure of $[Fe(CN)_6]^{-4}$, octahedral :


3d
4s
4p
Simple Fe^{+2} ion
$[Fe(CN)_6]^{-4}$
d^2sp^3 hybridization
CN CN CN CN CN CN

Structure of $[Ni(CN)_4]^{2-}$ ion :


3d
4s
4p
Simple Ni^{2+} ion
$[Ni(CN)_4]^{2-}$
dsp^2
CN CN CN CN

6. PARAMAGNETISM

Substances that are attracted into a magnetic field are said to be paramagnetic. The paramagnetism among elements and their compounds is due to the presence of unpaired electrons in the structure. The transition metals and their ions also contain unpaired electrons in partially filled d sub-shell and are, therefore, paramagnetic. The paramagnetism of d–block transition elements is due to the spin of the unpaired electron and the magnetic moment in Bohr magneton which can be calculated from the formula

$$\text{Spin magnetic moment} = \sqrt{n(n+2)}$$

where, n = number of unpaired electrons.

If the spin magnetic moment is determined experimentally, we can calculate the number of unpaired electrons in a complex by the above formula.

7. CATALYTIC PROPERTIES

Transition metals and their compounds possess good catalytic properties. For example Ni in the form of nickel formate is used as a catalyst in the hydrogenation of oils to produce artificial ghee. Other examples of the use of catalysts are V_2O_5 in the contact process of H_2SO_4 manufacture. Fe_3O_4 is used in the Haber Process for the manufacture of NH_3.

Some Individual Elements of the First Transition Series :

Chromium : The principal ore of chromium is chromite, $FeCr_2O_4$ or $FeO.Cr_2O_3$.

The metal may be obtained by the reduction of chromium trioxide. Cr_2O_3, with aluminium, by means of a method called Goldschmidt's aluminothermic process.

$$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$$

The reaction is highly exothermic. When dipped in nitric acid, the metal becomes "passive" i.e., it is rendered chemically inactive due to the formation of an oxide coating. Because of its brilliant lustre and resistance to corrosion, chromium is widely used as a plating material. It is extensively employed in the manufacture of various chrome steels, including "stainless" steel for alloys with nickel such as 'nichrome' and for plating iron to prevent rusting.

Chromium exhibits oxidation states of +2, + 3 and + 6. The compounds in which the metal shows an oxidation number of + 3 are the most stable, and those with the + 6 number are quite stable. The compounds of chromium in 'the +2 oxidation state are very unstable, and thus act as powerful reductants. It may be of interest to note that all compounds of chromium in these oxidation states are highly coloured. The chromous ion, Cr^{+2}, has a beautiful blue colour. The black chromous oxide, CrO, is basic; the green chromic oxide Cr_2O_3, is amphoteric, and the dark red chromic anhydride, CrO_3, is acidic.

The chromic anhydride, in which chromium shows its high oxidation state of +6, dissolves readily in water to form a strongly acid solution:

$$2CrO_3 + H_2O \longrightarrow H_2Cr_2O_7 \longrightarrow 2H^+ + Cr_2O_7^{-2}$$

Dichromic acid, $H_2Cr_2O_7$, exists only in solution. Its salts are called dichromates and contain the dichromate ion, $Cr_2O_7^{-2}$. Another acid which contains chromium in the +6 oxidation state is the chromic acid, H_2CrO_4. This acid, too, exists only in solution. Its salts, which are called chromates, contain the chromate ion, CrO_4^{-2}. On addition of an acid, the yellow chromate ion is converted to the orange-red dichromate ion:

$$2CrO_4^{-2} + 2H^+ \rightleftharpoons Cr_2O_7^{-2} + H_2O$$

The process can be reversed by the addition of a base:

$$Cr_2O_7^{-2} + 2OH^- \rightleftharpoons 2CrO_4^{-2} + H_2O$$

The chromate ion has a tetrahedral structure. In the dichromate ion, there are two tetrahedra linked together through a common oxygen atom.

The most important compound of manganese is potassium permanganate, $KMnO_4$, which contains manganese in 1 + 7 oxidation state. The salt has a deep purple-red colour and dissolves readily in water. It is a powerful oxidizing agent and is widely used in analytical chemistry. Generally, the MnO_4^- ion is reduced to the Mn^{++} ion in acid solutions, but to MnO_2 in basic solutions.

In acid medium, $KMnO_4$ is reduced to Mn^{+2} compounds. The change of oxidation state from Mn^{+7} to Mn^{+2} involves acceptance of 5 electrons by $KMnO_4$ state from Mn^{+7} to Mn^{+2} involves acceptance of 5 electrons by $KMnO_4$. The equivalent weight of $KMnO_4$ in acid medium is $\frac{1}{5}$ of the molecular weight.

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{+2} + 4H_2O$$

In acid medium some of the oxidation reactions are:

$$10FeSO_4 + 2KMnO_4 + 9H_2SO_4 \longrightarrow 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

$$5H_2SO_3 + 2KMnO_4 \longrightarrow 2H_2SO_4 + K_2SO_4 + 2MnSO_4 + 3H_2O$$

It is to be noted that in acid medium HCl and HNO_3 cannot be used since HCl is oxidized to Cl_2 by $KMnO_4$ and HNO_3 itself is an oxidizing agent. Hence H_2SO_4 is generally used for reactions in acid medium.

In alkaline medium, $KMnO_4$ changes to MnO_2 i.e. from Mn^{+7} to Mn^{+4} involve acceptance of 3 electrons. The equivalent weight of $KMnO_4$ in alkaline medium is $\frac{1}{3}$ of the molecular weight.

$$MnO_4^- + 2H_2O + 3e \longrightarrow MnO_2 + 4OH^-$$

Iron:

The element iron is industrially very important. It is very abundant, ranking fourth in the earth's crust after O_2, Si and Al. It occurs in nature in a variety of compounds. The most important ores are:

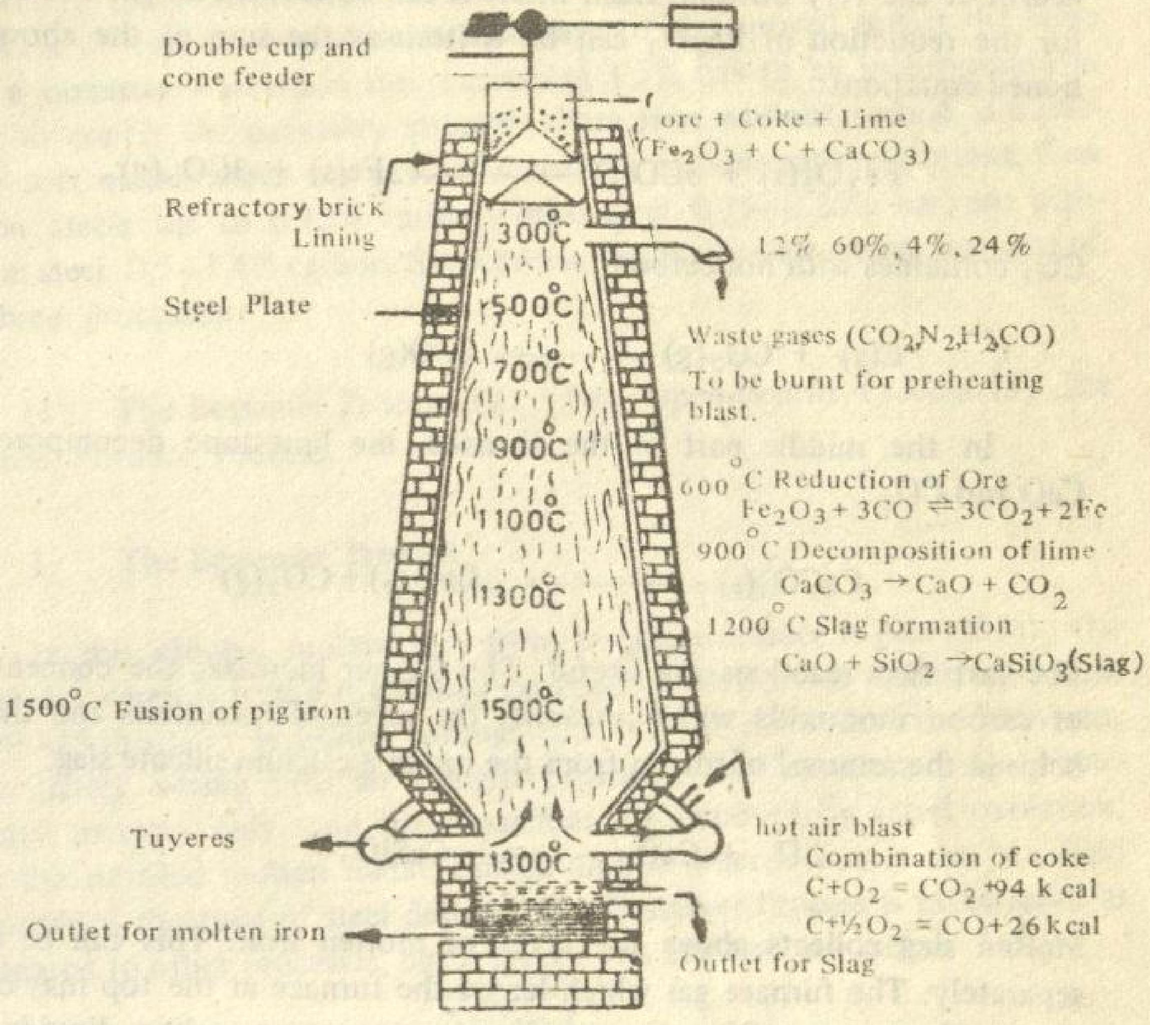

Double cup and cone feeder
ore + Coke + Lime
(Fe_2O_3 + C + $CaCO_3$)
Refractory brick Lining
300°C
12% 60%, 4%, 24%
Steel Plate
500°C
Waste gases (CO_2, N_2, H_2, CO)
To be burnt for preheating blast.
700°C
900°C
600°C Reduction of Ore
$Fe_2O_3 + 3CO \rightleftharpoons 3CO_2 + 2Fe$
1100°C
900°C Decomposition of lime
$CaCO_3 \rightarrow CaO + CO_2$
1300°C
1200°C Slag formation
$CaO + SiO_2 \rightarrow CaSiO_3$(Slag)
1500°C Fusion of pig iron
1500°C
Tuyeres
hot air blast
1300°C
Combination of coke
$C + O_2 = CO_2$ + 94 k cal
$C + \frac{1}{2}O_2 = CO$ + 26 kcal
Outlet for molten iron
Outlet for Slag

Fig. 10.4: The Blast Furnace

Then Fe_3O_4 further gets reduced to FeO

$$Fe_3O_4(s) + CO(g) \longrightarrow 3FeO(s) + CO_2(g)$$

Finally, towards the bottom of the furnace, FeO is eventually reduced to Fe

$$FeO(s) + CO(g) \longrightarrow Fe(s) + CO_2(g)$$

At the lowest part of the furnace the temperature is above the melting point of the impure iron, therefore, the solid melts and dips down into the hearth at the very bottom, from where it can be drawn out. The net equation for the reduction of Fe_2O_3 can be written as the sum of the above mentioned equations:

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$$

CO_2 combines with hot carbon

$$C(s) + CO_2(g) \longrightarrow 2CO(g)$$

In the middle part of the furnace, the limestone decomposes into CaO and CO_2.

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

The last two reactions are useful. The former increases the concentration of carbon monoxide which prevents the reversible reactions and the later helps in the removal of silicon from the ore as a calcium silicate slag.

$$SiO_2 + CaO \longrightarrow CaSiO_3$$

Molten slag collects above the layer of molten iron. This can be tapped separately. The furnace gas which leaves the furnace at the top may contain about 25 per cent CO, about 60%, nitrogen, some carbon dioxide and a little hydrogen. This is not very different from producer gas and can be employed for preheating the air to be blown in the furnace from the bottom. The molten iron is either run into an endless chain of metal moulds which are subsequently cooled by a spray of water or it is taken to the steel converter.

Carbon will dissolve in molten iron up to a saturation limit of about 4.5%. Other impurities will also be present. A typical cast iron from the blast-furnace would contain 3–4% carbon, up to 2% silica, 0.51% manganese, perhaps phosphorus up to 1.5% (depending on the ore that was used) and a little amount of sulphur (less than 0.1%). The cast iron is tough and strong and relatively cheap, but it is brittle and a blow will easily fracture it. Phosphorus and sulphur have some effect on the brittleness of the product, but the main reason for the undesirable quality is the presence of high percentage of carbon.

Steel-making:

To prepare steel with the necessary good qualities associated with this form of iron, unwanted impurities have to be removed and at the same time a quantity of carbon not exceeding 1.5% has to be incorporated in order to confer the necessary strength. Pure iron without carbon is a relatively soft metal. Steels are graded according to their carbon content. Low carbon steels up to 0.15% carbon; mild steel 0.15–0.25% carbon; high-carbon steel 0.5–1.4% carbon. Steel now-a-days are usually made by one of the three processes:

(1) The Bessemer Process (2) The Open-Hearth Process (3) The Electric Furnace Process.

1. The Bessemer Process :

In this process, molten iron from the blast-furnace is poured into the converter when it is in a horizontal position. A blast of air under a pressure of 20–25 lb/sq. in. is blown through the molten metal and the converter immediately swung into an upright position. The 'blow' lasts for about twenty minutes only, and the impurities are removed by rapid oxidation. To the purified molten metal, carbon and/or other elements can be added to produce the type of steel desired. The Bessemer Process is more rapid as compared to other processes, but it gives a less uniform product.

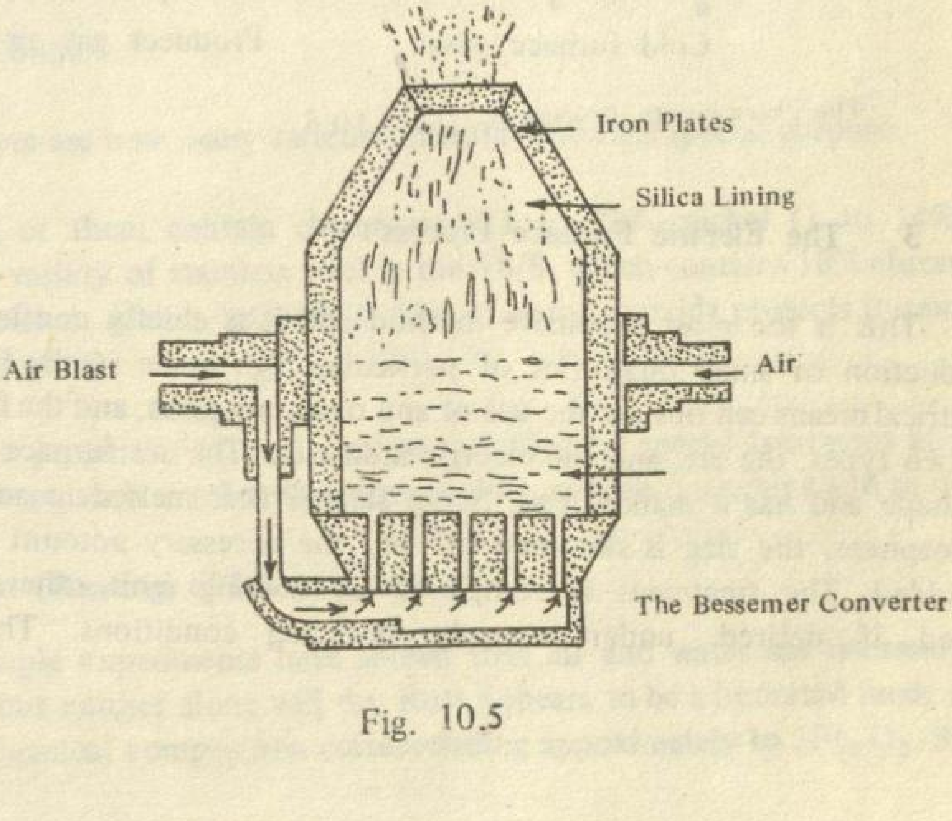
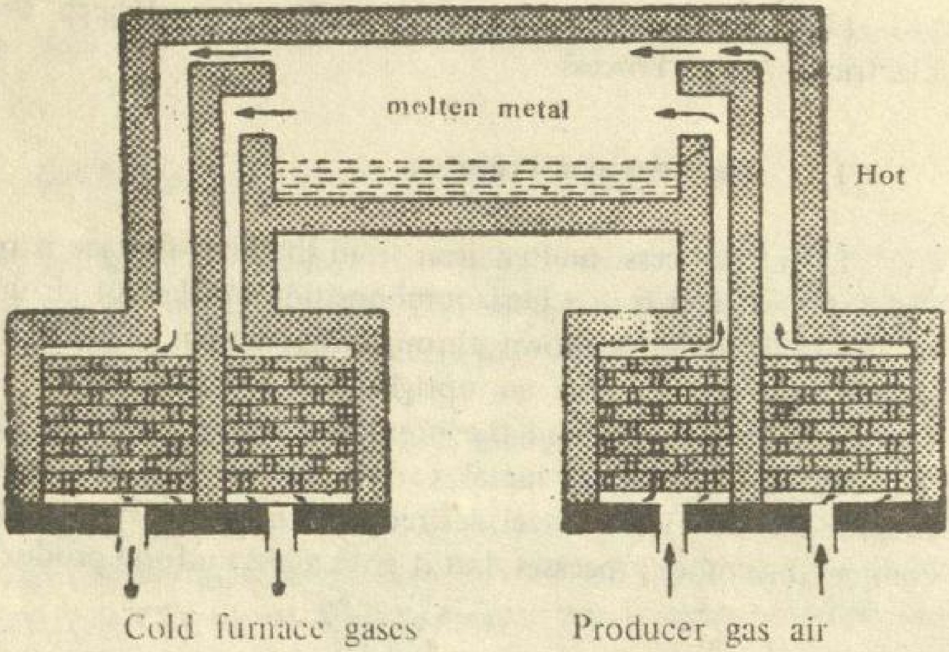


Fig. 10.5

2. The Open-Hearth Process :

This process takes a much longer time than the Bessemer Process but its great advantage is that it can handle all types of scrap. Cast iron and steel scrap are heated with Haematite (iron oxide) as an oxidizing agent on a large flat hearth of a Reverberatory furnace (Fig. 10.6). The necessary heat is provided by the combustion of gases (from oil or coal) above the surface of the charge. The direction of flow of the hot gases is reversed from time to time, and the escaping gas gives up its heat to the brickwork, which in turn preheats the gas when the flow is reversed. In the final stages, alloying elements, more carbon if necessary and deoxidizers may be added.



The Open-hearth Process Fig. 10.5.

3. The Electric Furnace Process :

This is the most expensive method and it is chiefly confined to the production of small quantities of particular high grade steels. Heating by electrical means can obviate the use of any oxidizing gases, and the furnaces are of two types: the arc, and the electric induction. The arc furnace is circular in shape and has a shallow bed. Scrap steel is first melted in an oxidizing atmosphere, the slag is skimmed off and the necessary amount of carbon is added. The treatment is completed by heating with other elements, added if desired, under strongly reducing conditions. The temper ature of the furnace may be as high as 3,400°C; and the electrodes are of carbon. Induction furnaces need no carbon electrodes and in them heat losses are minimized.

In Pakistan a small quantity of steel is manufactured by the electrical method from the imported cast iron, iron scrap and iron ore. A huge steel mill, is being set up at Karachi for the production of steel from the imported ore.

Special Steel :

There is a wide variety of steel for particular purposes; here a few of the commoner ones are listed with the approximate percentage composition by weight.

Manganese Steel :

Contains 7–20%of manganese. A very hard steel.

Silicon Steel :

Contains about 3½% silicon. Used for transformers.

Stainless Steel :

There are now many varieties manufactured for special purpose.

All of them contain chromium (11 to 22%) nickel (1 to 14%). A common variety of stainless steel is the 18/8, which contains 18% chromium and 8% nickel. A thin superficial film of chromic oxide protects the surface from corrosion.

The properties of steel may be modified by special treatment after its manufacture, such as reheating, slow cooling, sudden quenching and so on.

Corrosion (Rusting) of Iron and steel.

Simple experiments have shown that air and water are necessary for rusting, but neither alone will do. Rust appears to be a hydrated ferric oxide with a chemical composition corresponding appoximately to $2Fe_2O_3 . 3H_2O$.

However, since the water content is not always the same, it is preferable to write $Fe_2O_3xH_2O$. Rust may vary in colour from bright yellow, through shade of red or brown, to almost black. Rusting can be inhibited by covering the metal with a film of oil, painting the surface, electroplating, alloying to produce stainless steel, chemical treatment of the surface, addition of inhibitors such as sodium benzoate etc.

Nickel.

The two most important nickel ores are; pentalandite, NiS, 2FeS, and garnierite, $Ni.Mg.\ SiO_3H_2O$. Nickel also occurs in other complex sulphide copper ores usually containing small amount of nickel, which is removed in the electrolytic refining process.

Metallurgy :

The sulphide ores are converted to nickel oxide which involves a number of steps. The nickel oxide is reduced to metal by hydrogen.

$$NiO + H_2 \rightarrow H_2O + Ni$$

The nickel thus prepared is always mixed with cobalt. The two metals are separated by the *Mond's Process.* In this process a stream of CO is passed over the finely divided metals at about 60°C. Nickel forms a volatile, $Ni(CO)_4$ under these conditions. $Ni(CO)_4$ being volatile, distills over leaving a residue of cobalt.

$$Ni + 4CO \xrightarrow[\text{1 atmosphere}]{60^\circ C} Ni(CO)_4 \uparrow$$

On heating to 200°C the carbonyl decomposes to liberate free nickel.

$$Ni(CO)_4 \xrightarrow{200^\circ C} Ni + 4CO$$

Properties:

Nickel is a hard, silvery white metal. Nickel is less reactive than iron and cobalt. It is extremely resistant to oxidation. It usually exists in + 2 oxidation states in its compounds.

Nickel is used for making "tough" steels, for nickel plating, and as a catalyst for the hydrogenation of oil (Preparation of 'dalda' from the vegetable oil). It is also used in the coin making. Our coins from 25 pasia to a rupee denomination are made of a nickel-copper alloy.

Nichrome, an alloy of Ni, Cr, Fe and Mn, has a high melting point and a high electrical resistance. It is used in making heating elements for electrical appliances like heaters, irons and toasters.

Monel contains about 67% Ni and 28% Cu along with small amounts of Mn and Fe. It resists the action of air, water and acids. It is extensively used in chemical industries.

Copper :

Copper frequently occurs in the free state; and as a rule such deposits are small. The copper ores may be classified as:

1. **Sulphide ores** :

The important ores are chalcopyrite, $CuFeS_2$, bornite, Cu_5FeS_4 and chalcocite Cu_2S.

2. **Oxidized ores** :

Cuperite, Cu_2O, malaconite, CuO, malachite, $Cu_2(OH)_2CO_3$ and azurite, $Cu_3(OH)_2(CO_3)_2$ are the examples of the oxidized ores :

Metallurgy :

Sulphide ores of copper are the main source of the metal. These ores are usually low-grade and require *concentration* by oil-floatation process. The low-grade ore is ground very fine. Then mixed with water, oil and air to form a frothy mixture. The earthly impurities (gangue) get preferentially wetted by water and settle to the bottom, while the unwetted ore particles are carried to the surface in the froth of air bubbles. The froth is skimmed off to get the concentrated ore

The concentrated ore is partially *roasted* to get Cu_2S, FeS, FeO, and SO_2. Sulphur dioxide is converted into sulphuric acid.

$$\underset{\text{Chalcopyrite}}{4CuFeS_2} + 5O_2 \rightarrow 2Cu_2S + 2FeS + 2FeO + 4SO_2$$

The next step is *smelting.* The partially roasted ore is mixed with silica and lime and fused. The FeO is converted into a silicate slag.

$$FeO + SiO_2 \rightarrow FeSiO_3$$

The FeS and Cu_2S form a mixture known as *matte.* The slag floats on the surface of the matte and removed.

Production of Blister Copper :

After smelting, the matte is treated with a hot blast of air in a Bessemer Converter. A series of reactions take place in which copper is the final product.

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$

The copper produced in this way is called *Blister Copper.* This is because when copper cools, dissolved gases escape forming blisters. The blister copper is about 99% pure. It is usually purified by electro-refining.

Refining :

In electro-refining, sheets of pure copper are used as the cathodes in the electrolytic cells, and large plates of the blister copper are used as the anodes. The electrolyte is a solution of $CuSO_4$ in sulphuric acid. On passing the electric current the copper from the anode goes into the solution as Cu^{+2}, while Cu^{+2} ions are deposited as free copper on the cathode.

$$Cu \rightarrow Cu^{+2} + 2e \text{ (anode)}$$

$$Cu^{+2} + 2e \rightarrow Cu \text{ (cathode)}$$

Less electropositive metals like Ag and Au do not plate out and remain as *anode mud.* Electrolytic copper is over 99.9% pure.

Properties :

Copper is a soft ductile melleable red metal. Next to silver, it is the best conductor of electricity.

Copper shows two oxidation states in its compounds :

(1) Cuprous compounds in which the oxidation state of Cu is + 1, and (2) Cupric compounds in which the oxidation state of Cu is + 2. Copper (II) compounds being more stable, are much more common.

Cupric sulphate. $CuSO_4 \cdot 5H_2O$, also known as *blue vitriol,* is an important copper compound. It is used in electroplating, as a weed killer and to make the agricultural spray known as *Bordeaux mixture.*

Reaction of Cu^{+2} ion with Ammonia :

A solution of a cupric salt changes to a deep-blue colour when an excess of ammonia is added. This is due to the formation of the complex ion; $[Cu(NH_3)_4]^{+2}$.

$$\underset{\text{light blue}}{[Cu(H_2O)_4]^{+2}} + 4NH_3 \rightarrow \underset{\text{deep blue}}{[Cu(NH_3)_4]^{+2}} + 4H_2O$$

The hydrated cupric ions are light blue due to the presence of coordinated water molecule. On heating the water molecules are lost and the resulting product becomes colourless, *e.g.,*

$$\underset{\text{light blue}}{[Cu(H_2O)_4]^{+2}} \rightarrow \underset{\text{colourless}}{Cu^{+2}} + 4H_2O$$

(c) $[Cu(H_2O)_4]^{+2} \rightarrow$

(d) Reaction between $KMnO_4$ and HCl.

10. Name the important ore of chromium found in Pakistan. How would you convert the CrO_4^{-2} ion into $Cr_2O_7^{-2}$ and vice versa. Write the structure of these two ions.

11. Write the electronic configuration of :

Cr, Mn, Fe, Ni, Co, Cu and Zn.

12. What is steel? Describe one method for its preparation. Give examples of special steels.

13. Write balanced equations for.

(a) $Cr_2O_3 + Al \rightarrow$

(b) $Cu_2S + Cu_2O \rightarrow$

(c) $MnO_2 + HCl \rightarrow$

(d) $Ni + CO \rightarrow$

(e) $Fe_2O_3 + CO \rightarrow$

(f) $Cr_2O_7^{-2} + 2OH^- \rightarrow$

(g) $NiO + H \rightarrow$

CHAPTER 11

NOBLE GASES

Helium, Neon, Argon, Krypton, Xenon and Radon, which are known as Inert (or noble) gases, are placed in Group VIII A of the periodic table. These gases are placed in the group VIII of the periodic classification because they contain eight electrons in the outermost shell. They are also known as inert gases, because of their relative inertness.

Argon was the first inert gas discovered by Rayleigh and Ramsay in 1894. Ramsay shortly afterwards indentified the gas given off by Uranium minerals as the unknown element, Helium, whose existence Lockyer had postulated in 1868 to account for a prominent yellow line in the solar spectrum. Subsequent investigation by fractical distillation of the crude Argon obtained from air led to the discovery of Neon, Krypton and Xenon. The percentage by volume of the various gases in air being :

He	Ne	Ar	Kr	Xe
0.00052	0.0018	0.93	0.001	0.0008 per cent.

Research on radioactive elements has shown that the so-called alpha ray, or alphs particle, is doubly positively charged helium ion and that helium is thus one of the products of the decomposition of these unstable elements. The loss of an alpha particle by radium results in the formation of the inert gas group, Radon.

$$^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He}$$

Physical Properties :

The more important physical properties have been summerized in the table given below The gases are all monoatomic, and the low values of the boiling points indicate that their atoms have very little attraction for each other. The inert gases are somewhat soluble in water and the solubility increases markedly with increasing atomic weights.

Table 11.1

The Properties of Inert gases

	At.No.	Electronic configuration	I.P K Cal/mole	M.P °C	B.P °C
He	2	$1s^2$	562	–272	–269
Ne	10	$[He].\ 2S^2 2P^6$	497	–248	–246
Ar	18	$[Ne].\ 3S^2 3P^6$	363	–189	–186
Kr	36	$[Ar]\ 3d^{10}\ 4S^2\ 4P^6$	323	–157	–153
Xe	54	$[Kr]\ 4d^{10}.\ 5S^2\ 5P^6$	280	–111	–108
Rn	86	$[Xe]\ 4f^{14}.\ 5d^{10} 6S^2 6P^6$	247	–71	–62

Electronic Structure and Chemical Properties :

The configuration of the electrons in the various atoms of the group is important not only in explaining their relative inertness, but also in connection with the interpretation of the formation of the great majority of chemical compounds. Each inert gas marks the completion of an outer shell of eight electrons, except in the case of helium which contains two electrons. These completed groups are so stable that the ionization potentials of the inert gases are very high and they do not form chemical bonds readily.

Commercial Preparation and Uses :

Helium is prepared from natural gas by fractional liquefaction. Helium is useful as a gas for filling balloons and airships as it is non-inflammable. It is now employed as a coolant in nuclear reactors. Helium has assumed considerable importance in deep diving. The very low boiling point of helium makes it of special importance in the investigation of the behaviour of substances in the neighbourhood of absolute zero (–273°C).

The neon tubes used in electric signs contain the gas under low pressure. The commercial source of the element is the fractionation of atmospheric argon

Argon is now used extensively in filling electric light bulbs. The presence of the inert gas decreases the rate of evaporation of the filament, retards the blackening of the bulb and makes possible the operation of the lamp at a higher temperature, thus greatly increasing its efficiency.

Krypton and Xenon are very scarce and expensive; but they have been employed in small electric lamps for special purposes such as the miners cap lamp.

Radon has been used in medicine for the treatment of malignant growths.

Compounds of the Inert Gases :

Until recently, no chemical compounds of the inert gases were known.

Early work with Xenon hexafluoride showed that $XeOF_4$ resulted from the reaction between the hexafluoride and silica.

$$2XeF_6 + SiO_2 \rightarrow 2XeOF_4 + SiF_4$$

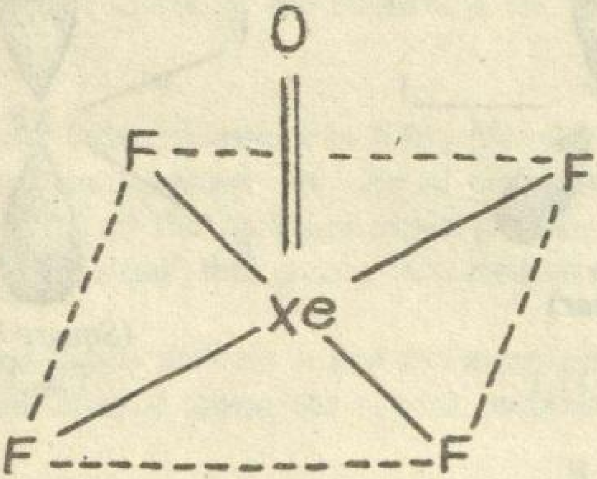
It is important to stop the reaction as soon as the XeF_6 is consumed since further reaction results in the formation of the explosive trioxide.

$$XeOF_4 + SiO_4 \rightarrow SiF_4 + XeO_3$$

A far better preparative method is the reaction of Xenon haxafluoride with an equimolar quantity water

$$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$$

At room temperature $XeOF_4$ (Xenon-Oxy tetrafluoride) is a clear, colourless mobile liquid. The molecule has a square pyramid structure with the oxygen at the apex of the pyramid while the Xenon atom is coplanar with fluorine atoms.



The hydrolysis reactions of Xenon difluoride, Xenon tetrafluoride and hexafluoride result in the oxides of Xenon. The reactions are represented in the simplest terms by the equations below :

$$XeF_2 + H_2O \rightarrow Xe + \frac{1}{2}O_2 + 2HF$$

$$3XeF_4 + 6H_2O \rightarrow XeO_3 + 2Xe + 1\frac{1}{2}O_2 + 12HF$$

$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$

QUESTIONS

1. Give an account of the way in which a knowledge of the properties and electronic structures of the rare gases has been of use in advancing our understanding of valency and the periodic system of elements.

2. The atomic number of the inert-gases are 2, 10, 18, 36, 54 and 86. Make use of this information in deducing ;

(a) The properties of the elements having atomic numbers 15 and 56.

(b) The salient characteristics of the newly discovered elements astatine (at. No 85) and francium (at. No. 87).

3. Draw the electronic structures of the fluorides, Oxyfluorides and Xenon trioxide.

CHAPTER 12

INTRODUCTION TO ORGANIC CHEMISTRY

Chemistry is mainly divided into three branches, namely Physical Chemistry, Inorganic Chemistry and Organic Chemistry. Originally Organic Chemistry was considered to be the study of the substances obtained from living organisms. It was believed that organic compounds can be synthesised only in living organisms and could not be synthesised in the laboratories from inorganic compounds. Until about 1850 chemists believed that vital force present in living organism was essential for synthesising the organic compounds. Since vital force could not be isolated from the living organisms so it was out of question to synthesise organic compound in the laboratory. In 1828 Wohler obtained a typical organic compound, urea, by heating an inorganic compound ammonium cyanate (NH_4CNO).

$$\underset{\text{Ammonium Cyanate}}{NH_4CNO} \xrightarrow{\text{heat}} \underset{\text{Urea}}{H_2N.CO\,NH_2}$$

Urea was hitherto obtained from urine of animals. Thus the historic synthesis of urea started the disintegration of vital force theory. By 1850 strong evidences were obtained to prove that vital force was not necessary for the synthesis of organic compounds as some organic compounds like urea, methane and acetic acid could be synthesised in laboratories from typical inorganic substances. In this way Organic Chemistry completely lost its original meaning. However, for convenience the division between organic and inorganic compounds was retained. The common feature found in organic compounds was that all the organic compounds contain carbon. Therefore, organic chemistry is now defined as the chemistry of carbon compounds. Some carbon containing compounds like CO, CO_2 carbonates and bicarbonates are not included in Organic Chemistry but are studied in Inorganic Chemistry. Although many organic compounds are isolated from plants and animals, most of the organic compounds are synthesised in the laboratories.

Now an important question is that why carbon containing compounds are studied in a separate branch of Chemistry. The simple answer is that carbon containing compounds are about ten times more than compounds containing no carbon. There are about one million organic compounds and thousands of new organic compounds are being synthesised each year. Thus huge number of organic compounds justified their study in a separate branch of Chemistry. About 90% of the known organic compounds are synthesised in laboratories while the others are obtained from natural sources.

The next important and logical question arises, why carbon makes such a large number of compounds and what is the basic property which distinguishes carbon from rest of the elements.

This is due to the unique property of carbon that a large number of its atoms can attach themselves forming straight chains, branched chains and rings of many sizes. The bonds between carbon atom and the atoms of other elements are also quite stable. In this respect no other element can compete carbon. Hydrogen is most frequently attached to carbon atoms in organic compounds. There are only a few organic compounds having no hydrogen. The elements oxygen, nitrogen, sulphur and halogens are also frequently present in organic compounds.

Sources of Organic Compounds :

Petroleum, natural gas and coal are the most important sources of organic compounds. These substances may be regarded as products of decay of animals and plants. Petroleum and natural gas are the sources of aliphatic hydrocarbons, while coal is the main source of aromatic compounds.

Organic compounds are also obtained from plants and animals. Carbohydrates, proteins, oils, etc. are examples of organic compounds found in plants and animals. A fairly large number of organic compounds are also synthesised from inorganic compounds.

Importance of Organic Chemistry :

Organic Chemistry is of great importance to our every day life. The basic necessities of life such as food and clothing are essentially organic susbtances. Most of the substances used in medicine, agriculture and industry are organic in nature. Examples of some useful organic compounds are dyes, paper, explosives, inks, paints, plastics, drugs and gasoline. All the living organisms are mainly made up of organic compounds and water. Actually life itself is a series of organic reactions.

Main differences between Organic and Inorganic Compounds :

The chief differences between the properties of organic and inorganic compounds arise due to the fact that organic molecules are constituted mainly by covalent bonds while ionic bonds are very common in inorganic molecules. Inorganic compounds are good electrolytes while organic compounds are not. Inorganic compounds are generally high melting solids or high boiling liquids, but organic compounds are low melting solids or low boiling liquids. Most of the organic compounds decompose at high temperature (below 900°C) while most of the inorganic compounds can withstand high temperatures without decomposition. Inorganic compounds are soluble in highly polar solvents such as water, while organic compounds are usually soluble in non-polar organic solvents. Inorganic reactions being ionic in nature take place almost instantaneously but organic reactions proceed much more slowly as they require the breaking and formation of covalent bonds.

QUESTIONS

1. Classify the following into organic and inorganic compounds.

$NaCl$; CH_4; C_2H_5OH; HCl; CCl_4; $CHCl_3$; K_2HPO_4; $Fe_2(SO_4)_3$; CS_2

$C_6H_{12}O_6$; $C_2H_5NH_2$; $C_2H_5SC_2H_5$; CH_3OCH_3; C_2F_6; $NaHCO_3$; CO_2

and HCN

2. Give various possible arrangements for the following.

$C_2, C_6, C_7, C_8, C_{10}$.

3. Which of the following substances are mainly organic and which are mainly inorganic :

Rocks; Clothes; Wood; Bricks; Cement; Soap; Meat; Petroleum, Glass; Paper; Explosives; Oils; Bread; Plastics; Steel; Sand; Flowers; Diamond.

4. Which of the following statements are correct and which are wrong.

(i) All organic compounds have carbon.

(ii) All compounds having carbon are organic compounds.

(iii) An organic compound must have hydrogen.

(iv) Organic compounds may be synthesised from inorganic susbtances.

(v) Carbon atoms cannot be linked together in cyclic structure.

(vi) Organic compounds contain only carbon.

(vii) Organic reactions are slower than inorganic reactions.

(viii) Organic compounds are usually stable towards high temperatures (500°C).

(ix) Plants and animals are mainly composed of organic material.

(x) Vital force is necessary for synthesising organic compounds.

(xi) Life is possible without organic reactions.

(xii) All organic compounds existing in nature have been isolated and identified.

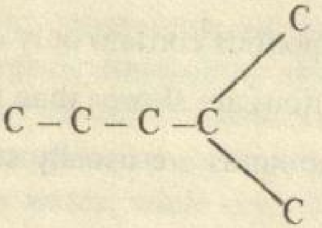
5. How will you account for such a large number (more than a million) of organic compounds.

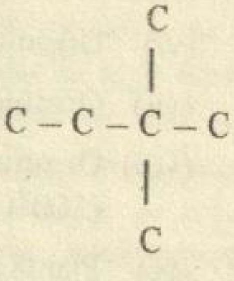
CHAPTER 13

STRUCTURE, CLASSIFICATION AND REACTIONS OF ORGANIC COMPOUNDS

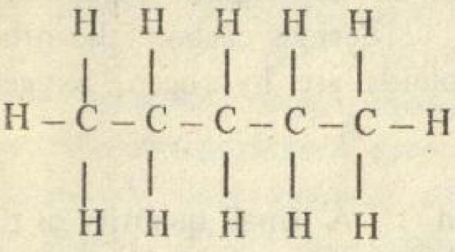
Organic Chemistry is actually based on structural theory. Structural theory brings together and arranges in a systematic way the millions of facts of thousands of individual organic compounds. Compounds having similarity in their structures also have similarity in their physical and chemical properties. Knowing the structures of an organic compound one can predict its properties as well as its methods of preparation. Carbon atoms can attach themselves in different ways forming open chains and rings which may have branches and cross links. Therefore, for a given number of carbon atoms several arrangements are possible and each arrangement will show its own characteristic set of physical and chemical properties. For example, six carbon atoms can give several different arrangements and a few of them are shown below :

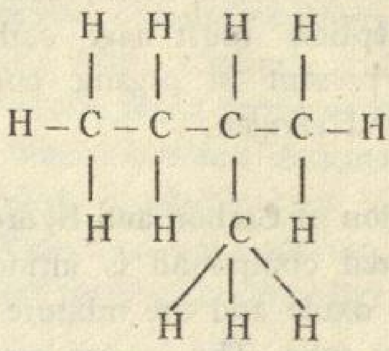
$C-C-C-C-C-C$;

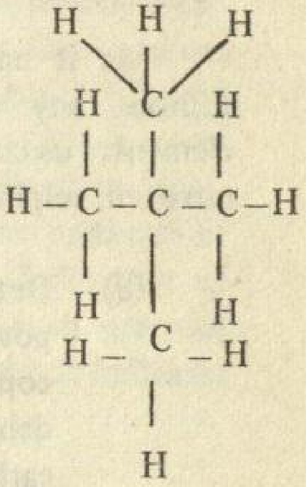




A molecule is represented by a *Molecular Formula* which tells the actual number of atoms of different elements present in the molecule. A given molecular formula can represent a number of different organic compounds. For example molecular formula C_5H_{12} represents three compounds, and there are 120 known compounds with the molecular formula $C_{10}H_{16}O$.







Different compounds having same molecular formula are called *isomers* (iso-same ; mer = units) and this phenomenon is called *isomerism*. Isomers have different sets of physical and chemical properties. Isomerism is very much common in organic chemistry as compared to inorganic chemistry. Due to this Isomerism it is not sufficient to simply know the molecular formula of an organic compound but the knowledge of the structure of that compound is also essential. Therefore, the most important job of an organic chmist is to determine the structure of an organic compound. It is quite obvious that in determining the structure of a compound the first step will be to find out the molecular formula of the compound.

Determination of molecular formula : Determination of molecular formula involves the following steps (1) Qualitative analysis to determine the kinds of elements present in the compound. (2) Quantitative analysis to determine the percentage composition of the compound in term of elements present. (3) Calculation of Empirical Formula. *Empirical formula indicates the relative number of atoms of different elements present in a molecule of the compound* (4) Determination of Molecular Weight, (5) Calculation of Molecular Formula.

(1) Qualitative Analysis ;

As it has already been mentioned that all the organic compounds without any exception must have carbon. Besides carbon, the other elements usually present in organic compounds are hydrogen, oxygen, nitrogen, sulphur and halogen.

(*a*) **Detection of Carbon and Hydrogen** : A small quantity of the powdered compound is intimately mixed with dry powdered copper oxide and the mixture is heated in a tube fitted with a delivery tube. The issuing gases are passed into lime water. If carbon is present in the compound it will be oxidised to carbon dioxide which will turn lime water milky. If hydrogen is present small drops of water will appear on the upper portion of test tube.

$$C + O_2 \longrightarrow CO_2$$

$$2H_2 + O_2 \longrightarrow 2H_2O$$

(*b*) **Detection of Nitrogen, Sulphur and Halogens (Lassaigne Test)**: In this test an organic compound is fused with metallic sodium. For this purpose a small piece of metallic sodium is first melted in a small hard test tube until the vapour rises in the tube. Then a very small quantity of organic compound is dropped over it and heated first gently and then strongly until the tube becomes red hot. The tube is then immediately plunged into distilled water (about 10 ml.) contained in a small mortar and is covered with a clean wire gauze. After the reaction is over, the mixture is ground to extract sodium salts thoroughly. The contents are transferred to a porcelein basin and heated to boiling and filtered. This filtrate is known as Lassaigne's solution and is used for testing nitrogen, sulphur and halogens.

If nitrogen, sulphur and halogens are present in the compound they will be converted into ionizable sodium cyanide, sodium sulphide and sodium halides respectively. Now the usual ionic tests of inorganic qualitative analysis are applied to identify these acid radicals.

Nitrogen : Ferrous sulphate crystals (about 0.2 gm) are added to alkaline Lassaigne's solution. Dark greenish grey precipitate of ferrous hydroxide is formed. The mixture is boiled for a few minutes to form sodium ferrocyanide. After cooling the mixture, one drop of ferric chloride solution is added to it and then acidified with dilute sulphuric acid. Sodium ferrocyanide reacts with ferric chloride to form ferric ferrocyanide (Prussian blue). Thus the appearance of greenish blue coloration indicates the presence of nitrogen. If only greenish coloration is obtained, it is an indication of insufficient reaction of organic compound with sodium. If such greenish solution on filtration leaves deep blue particles on the filter paper, it indicates the presence of nitrgoen.

$$6NaCN + Fe(OH)_2 \longrightarrow Na_4[Fe(CN)_6] + 2\,NaOH$$

$$3Na_4[Fe(CN)_6] + 4\,FeCl_3 \longrightarrow \underset{\substack{\text{Ferriferocyanide} \\ \text{(Prussian blue)}}}{Fe_4[Fe(CN)_6]_3} + 12\,NaCl$$

Sulphur : Sulphur may be tested by the following methods :

(*i*) Lassaigne's solution is acidified with dilute acetic acid. A few drops of lead acetate solution are added. A black precipitate of lead sulphide indicates the presence of sulphur.

$$Na_2S + Pb(CH_3COO)_2 \longrightarrow PbS\downarrow + 2\,CH_3COONa$$

(*ii*) A few drops of freshly prepared dil aqueous solution of sodium nitroprusside is added to Lassaigne's solution.

A brilliant purple colouration indicates sulphur.

Halogens : Two procedures may be adopted for testing halogens depending upon whether nitrogen and sulphur are present or absent.

(*i*) **Nitrogen and Sulphur Absent** : Lassaigne's solution is acidified with dil. nitric acid. Then excess of silver nitrate solution is added. A white or yellow precipitate indicates the presence of halogens. A white precipitate soluble in ammonium hydroxide indicates chlorine, a pale yellow precipitate soluble with difficulty in ammonium hydroxide indicates bromine and a yellow precipitate insoluble in ammonium hydroxide indicates iodine.

$$NaX + AgNO_3 \longrightarrow AgX + NaNO_3$$

(*ii*) **Nitrogen and /or Sulphur Present :** In such a case addition of silver nitrate to Lassaigne's solution will give precipitates of silver cyanide and silver sulphide along with the precipitate of silver halide (if halogen present). Therefore, it is necessary to remove cyanide and sulphide from Lassaigne's solution before adding silver nitrate. For this purpose Lassaigne's solution is made just acidic with dil. Nitric acid. It is transferred to an evaporating dish and boiled to expel hydrogen cyanide and hydrogen sulphide until half the original volume is left. Then halogens are tested as in method (i).

(2) **Quantitative Analysis :**

(*a*) **Estimation of Carbon and Hydrogen :** An accurately weighed quantity of organic compound is placed in a small boat. The small boat is then heated in a combustion tube in a stream of oxygen. Part of the combustion tube is packed with copper oxide.
Products of incomplete combustion get completely oxidised into carbon dioxide and hydrogen into water. The products issuing from the combustion tube are passed through the weighed tubes containing anhydrous magnesium perchlorate and soda-lime. Anhydrous magnesium perchlorate absorbs water while soda-lime absorbs carbon dioxide. After complete absorption these tubes are again weighed to find out the weight of water and carbon dioxide produced from the weighed quantity of organic compound. As we know that :

1 mole of CO_2 (44 g.) $\equiv$ 1 mole of C (12 g.) and 1 mole of H_2O (18 g.) $\equiv$ 1 mole. of H_2(2g.), so the percentage of carbon and hydrogen can be calculated in the original compound as shown in examples below :

Example 1. 1.2450 g. of an organic compound gave on combustion 1.837 g. of CO_2 **and 0.657 g. of H_2O. Calculate the percentage of carbon and hydrogen in the compound.**

44 g. of CO_2 $\equiv$ 12 g. of C

evolved in the free state. The tube is also packed with copper spiral to reduce any oxides of nitrogen (that may have been produced) into elementary nitrogen. The exit of the tube is attached to gas measuring burette known as nitrometer. This nitrometer is filled with 50% potassium hydroxide. The liberated nitrogen is swept with a stream of carbon dioxide and the issuing gases are led to nitrometer where potassium hydroxide absorbs carbon dioxide and nitrogen is collected. The collected volume of nitrogen is converted to standard temperature and pressure. As we know that weight of 22,400 ml. of nitrogen gas at standard temperature and pressure is one mole (28 g.) so the amount of nitrogen can be calculated in the sample.

Example 3. 0.0474 g. of an organic compound yielded 4.42 ml of nitrogen at 18°C and 754 m.m. pressure. Calculate percentage of nitrogen in the compound.

$$\text{Volume of nitrogen at standared temperature} = \frac{754 \times 273 \times 4.42}{760 \times 291} = 4.11 \text{ ml.}$$

$$\text{Wt. of nitrogen evolved} = \frac{28}{22400} \times 4.11 = 0.0051 \text{ g.}$$

$$\% \text{ of Nitrogen in the compound} = \frac{0.0051}{0.0474} \times 100 = 10.75$$

(*ii*) **Kjeldahl Method** : This method is based on the fact that when nitrogen containing organic compound is heated with conc. sulphuric acid, nitrogen of the compound is converted into ammonium sulphate. Alkaline solution of ammonium sulphate on distillation yields ammonia. This method is particularly applicable to biological materials. Kjeldahl method is not applicable to azo compounds and compounds containing nitrogen attached to oxygen such as nitro compounds.

A weighed quantity of nitrogen containing compound is strongly heated with conc. sulphuric acid in a Kjeldahl flask until the solution becomes colourless. This process is known as digestion. The mixture is, then transferred to a distillation apparatus. The mixture is made alkaline and the liberated ammonia distilled into excess of a standard acid solution.

The quantity of unreacted acid is determined by titration against a standard alkali. The amount of ammonia liberated from the sample can be calculated from the amount of acid neutralized by it. From this the percentage of nitrogen is calculated.

Example 4. Ammonia yielded from 0.0406 g. of an organic compound was passed into 21 ml Of N/20 sulphuric acid. The excess of acid required 15 ml. of N/30 NaOH for neutralization. Calculate the percentage of nitrogen in the compound

Volume of N/30 NaOH used for the neutralization of unacted acid = 15 ml.

Volume of N/20 H_2SO_4 used for the neutralization of NaOH can be calculated as follows :-

$$n_1 v_1 = n_2 v_2 \ , \ \frac{1}{30} \times 15 = \frac{1}{20} \times v_2 \ :$$

$$v_2 = \frac{1}{30} \times 15 \times 20 = 10 \text{ ml.}$$

Hence volume of N/20 H_2SO_4 neutralized by ammonia = 21 – 10 = 11 ml.

11 ml. of N/20 H_2SO_4 = 11 ml of N/20 NH_3 solution

$$\text{Amount of nitrogen in the compound} = \frac{14 \times 11}{20 \times 1000} = 0.0077 \text{ g.}$$

$$\therefore \quad \% \text{ of Nitrogen in the compound} = \frac{0.0077}{0.0406} \times 100 = 18.9$$

(*c*) **Estimation of Halogens (Carius's Method) :** The basic principle of this estimation is that halogen containing organic compound on heating with concentrated nitric acid in presence of silver nitrate gives the precipitate of silver halide.

A mixture of weighed organic compound, fuming nitric acid and silver nitrate is sealed in a thick-walled tube. The sealed tube is heated at about 280°C in a furnace for several hours. The precipitate of silver halide thus formed is taken out, washed, dried and weighed. From the weighed quantity of silver halide amount of halogen in the compound can be calculated.

1 Mole of silver halide = 1 Mole of halogen

Example 5 . 4.96 g. of an organic compound gave 5.0 g. of silver chloride, in the compound.

143. 4 g. of AgCl = 35. 5 g. of Cl_2 (108 + 35. 5)

$$\therefore \quad 5 \text{ g. of AgCl} = \frac{35.5}{143.4} \times 5 = 1.238 \text{ g. of Cl}$$

% of Cl_2 in the compound $= \frac{1.238}{4.96} \times 100 = 24.95$

(*d*) **Estimation of sulphur (Carius's Method)** Sulphur containing organic compound is strongly heated with fuming nitric acid in a sealed Carius tube for several hours. Nitric acid oxidises the sulphur of the compound into sulphuric acid. After heating, the contents of the tube are taken out and sulphuric acid produced is precipitated as barium sulphate by adding excess of barium chloride solution. Amount of sulphur can be calculated from the weight of the precipitated barium sulphate.

$$1 \text{ mole of } BaSO_4 \equiv 1 \text{ mole of S}$$

Example 6. 0.1280 g. of an organic compound yielded 0.135 g. of Barium sulphate. Calculate the percentage of sulphur in the compound.

233 g. of $BaSO_4 \equiv 32$ g. of S.

$$\therefore \quad 0.135 \text{ g. of } BaSO_4 \equiv \frac{32}{233} \times 0.135 = 0.0183 \text{ g. of S}$$

% of sulphur in the given compound $= \frac{0.0183}{0.1280} \times 100 = 14.29$

(*e*) **Percentage of Oxygen** There is no satisfactory method for estimation of oxygen. Usually percentage of oxygen is calculated by difference. Percentage of all the elements other than oxygen in the compound is added. If the total comes equal to 100, it shows the absence of oxygen and if the total is less than 100, the difference is the percentage of oxygen.

3. Calculation of Empirical Formula.

As mentioned earlier empirical formula indicates the simple ratio of atoms of different elements present in one molecule of the compound. For example empirical formulae of hydrogen peroxide, ethane, benzene and glucose are H_1O_1, C_1H_3, C_1H_1 and $C_1H_2O_1$ respectively while their molecular formulae are H_2O_2, C_2H_6, C_6H_6 and $C_6H_{12}O_6$ respectively. The molecular formula of a compound is a simple multiple of its empirical formula. Calculation of empirical formula can be divided into following four steps:

(*i*) Calculate the percentage of each element present in a compound.

(*ii*) Percentage composition of a compound gives us the relative weights of different elements per hundred parts by weight of the compound. To calculate the relative atomic ratios, percentage of each element is divided by its corresponding atomic weight.

(*iii*) To have the simple atomic ratios of all the values (iv) If the values obtained in step (iii) are not whole number or very close to whole numbers, convert them into whole numbers by multiplying each of them by the smallest possible number.

These four steps will become clear by the following examples.

Example 7. An organic compound on analysis was found to contain C = 68.80% and H = 3.44% Calculate the empirical formula of the compound.

(*i*) C = 68.80 % ; H = 3.44 %

% of O = 100 − (68.80 + 3.44) = 27.76

(*ii*) Relative atomic ratios :

$$C = \frac{68.8}{12} = 5.74 \ ; \ H = \frac{3.44}{1} = 3.44 \ ; \ O = \frac{27.76}{16} = 1.73$$

(*iii*) Simple atomic ratios :

$$C = \frac{5.74}{1.73} = 3.32 \ ; \ H = \frac{3.44}{1.73} = 2.01 \ ; \ O = \frac{1.73}{1.73} = 1$$

(*iv*) Carbon atoms are in fraction and, therefore, to convert them into whole number, multiply each value obtained in step (iii) by 3.

C = 3.32 x 3 = 9.96 = 10 ;
H = 2.01 x 3 = 6.03 = 6
O = 1 x 3 = 3

Empirical formula of the compound is $C_{10}H_6O_3$.

Example 8. In an organic compound carbon was found to be 80% and hydrogen 20 % . Find out the empirical formula of the compound.

(*i*) % of O = 100 – (80 + 20) = 0

(ii) Relative atomic proportions

$$C = \frac{80}{12} = 6.66 \; ; \; H = \frac{20}{1} = 20$$

(*iii*) Simple atomic proportions

$$C = \frac{6.66}{6.66} = 1 \; ; \; H = \frac{20}{6.66} = 3.03 = 3$$

Since the atomic ratios are in whole numbers there is no need of step (*iv*). Empirical formula of the compound is C_1H_3.

(4) Molecular Weight.

Molecular weight of organic compounds are usually determined by physical methods. Molecular weights, especially those of organic bases may also be determined by chemical methods.

Physical Methods : The following physical methods are generally used for determining the molecular weight of an organic compound :

(*i*) **Vapour Density (Victor Meyer's Method) :** This method requires small quantity of organic compound and gives accurate results. A known weight of the compound is volatilised at the lower close end of a hot tube. The vapours of the compound displace equivalent volume of hot air. The air thus displaced is collected through a delivery tube in a graduated cylinder over water. The volume of vapours of the compound is equal to the volume of air displaced. Note the pressure and temperature at which the air has been collected. From this we can calculate the volume of vapour of the compound at standard temperatre and pressure.

22.4 litres of any gas at S.T.P. = 1 mole of that gas. By using this relationship molecular weight of the compound can be calculated.

Example 9. 0.4240 g. of an organic compound on volatilisation displaced 65.6 ml. of air at 14.5°C and 744.5 m.m. pressure. Calculate the molecular weight of the compound. (Vapour pressure of water at 14.5°C = 12.3 m.m.).

65.6 ml. of displaced air = 65.6 ml. of vapours of the compound.

$$\text{Volume of vapours at S.T.P.} = \frac{(744.5 - 12.3) \times 273 \times 65.6}{287.5 \times 760} = 60.0 \text{ ml.}$$

60.0 ml. of vapours at S.T.P. weigh = 0.4240 g.

$$\therefore \quad 22{,}400 \text{ ml. vapours at S.T.P.} = \frac{0.4240}{60} \times 22400 = 158.2 \text{ g.}$$

Molecular weight of the compound is 158.2

(*ii*) Molecular weight by Elevation of the boiling point.

(*iii*) Molecular weight by Depression of the freezing point.

These two methods you have already studied in Part I of this book.

(iv) Molecular weight by Depression of the Freezing Point of Camphor (Rast's Method).

The basic principle of this method is the same as that of method (iii). In this method the organic substance is dissolved in molten camphor instead of some organic solvent. Due to very high molecular depression constant, 400, of camphor a given weight of a particular organic compound will give a much greater depression in camphor than in usual organic solvents. The further advantages of this method are that much smaller quantities of solute and camphor are required ; an ordinary thermometer can be used instead of a Beckmann thermometer and simple melting point apparatus may be used. This method consists of determining the molecular depression constant of camphor using pure naphthalene as solute. Molecular depression constant of camphor is the depression in its melting point caused by dissolving one mole of an organic substance in 100 g. of camphor. Then the depression in freezing point of camphor is determined using the unknown sample.

First the melting point of a pure sample of camphor is determined. A pure sample of naphthalene (about 0.2 g.) is accurately weighed in small tube, then about 2.0 g. of pure camphor is added into this tube. The tube is again weighed to know the exact weight of the added camphor. The tube is sealed to prevent the loss of either substance by volatilization. The camphor is melted by gently heating the tube. The molten material is mixed together by swirling the tube. After cooling, the contents of the tube are taken out and ground well to ensure a homogenous mixture. A portion of this mixture is filled in a capillary tube and the melting point of the mixture is determined by heating it very slowly. The difference between the melting point of Pure camphor and that of mixture is the depression in the melting point of camphor. Molecular depression constant (K) of camphor is calculated from the following equation :

$$K = \frac{\Delta t \times 128 \times W}{w \times 100}$$

Δt = Observed depression in melting point : 128 = Mol. wt. of naphthalene. W = weight of camphor, and w = weight of naphthalene.

The experiment is repeated as above but by using now the given organic substance instead of naphthalene and the depression (Δt) in the melting point of camphor is determined. Molecular weight (M) of the given sample is calculated in the following manner :

$$M = \frac{K \times w_1 \times 100}{W_1 \times \Delta t_1}$$

w_1 = weight of given sample ; W_1 = weight of camphor and Δt_1 = observed depression.

Example 10. 0.1990 g. of naphthalene was dissolved in 2.0590 g. of molten camphor . The resultant mixture melted at 146.5°C. A homogenous mixture containing 2.0705 g. of Camphor and 0.2053 g. of an unknown organic compound melted at 147.0°C. Calculate the molecular weight of unknown organic compound (M.P. of camphor is 176.0°C and mol. wt. of naphthalene is 128).

Molecular Depression Constant (K) of Camphor :

Depression in the melting point (Δt) = 176.0°C – 146.5°C =29.5°C

$$\therefore \quad K = \frac{29.5 \times 128 \times 2.0590}{0.1990 \times 100} = 391$$

Molecular weight of given compound :

Depression in the melting point (Δt_1) = 176.0 – 147.0 = 29.0°C.

$$\text{Molecular weight} = \frac{391 \times 0.2053 \times 100}{2.275 \times 29} = 133$$

(5) Molecular Formula :

As mentioned earlier molecular formula of a compound is a simple multiple of its empirical formula and similarly molecular wt. of a compound can be obtained by multiplying its empirical formula weight by some whole number.

Molecular formula = n x Empirical formula.

Where n is a whole number (1, 2, 3..............). This "n" can be calculated from the molecular weight and empirical formula weight of the compound.

$$n = \frac{\text{Mol. Wt.}}{\text{Empirical formula wt.}}$$

Thus knowing the empirical formula and mol. wt. of a compound its molecular formula can be readily calculated.

Example 11. A dibasic organic acid contains 26.6% carbon and 2.2% hydrogen. Its molecular weight is 92. Find out the molecular formula of the acid.

Calculation of empirical formula :

(*i*) % of O = 100 – (26.6 + 2.2) = 71.20

(*ii*) **Relative atomic proportions :**

$$C = \frac{26.6}{12} = 2.21 \; ; \; H = \frac{2.20}{1} = 2.20 \; ; \; O = \frac{71.20}{16} = 4.44$$

(*iii*) **Simple Atomic Proportion :**

$$C = \frac{2.21}{2.20} = 1 \;;\; H = \frac{2.20}{2.20} = 2.20 \;;\; O = \frac{4.44}{4.20} = 2.01 \text{ say } 2$$

Empirical formula of the acid = $C_1H_1O_2$

Molecular Formula : Molecular formula = n x Empirical formula

$$n = \frac{\text{Mol. Wt.}}{\text{Empirical formula weight}}$$

In this case empirical formula weight = 12 + 1 + 32 = 45

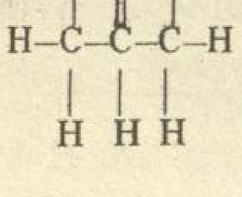
$$\therefore \quad n = \frac{92}{45} \equiv 2.04 \text{ say } 2$$

It has been mentioned earlier that n should be a whole number and if its calculated value is fractional, the nearest whole number should be taken.

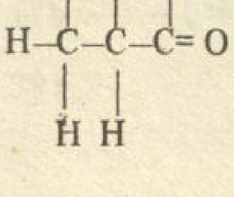
Molecular formula of the acid = 2 x $C_1H_1O_2$ = $C_2H_2O_4$

Structural Formula : After knowing the molecular formula of a given compound the next and the most difficult job of an organic chemist is to determine the structure of the compound. For a given molecular formula of a compound , usually several possible strucures may be written keeping in view that valency of each element present in the molecule is satisfied. An example of several possible structures with the same molecular formula has been described on page 193 where with the molecular formula C_5H_{12} three different structures are possible. Out of these possible structures the final selection of one structure for the compound will be done by studying the physical and chemical properties as well as by its synthesis.

Another example of the isomeric compounds having the molecular formula C_3H_6O but different structural formula is of acetone and propionaldehyde :



$$H\!-\!\overset{H}{\underset{H}{C}}\!-\!\overset{O}{\underset{H}{C}}\!-\!\overset{H}{\underset{H}{C}}\!-\!H$$

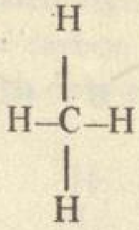


$$H\!-\!\overset{H}{\underset{H}{C}}\!-\!\overset{H}{\underset{H}{C}}\!-\!\overset{H}{C}\!=\!O$$

Classification of Organic Compounds : Organic compounds are divided into the following main groups :

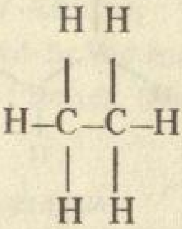
1. **Aliphatic Compounds** : All the organic compounds with an open chain of carbon atoms are known as aliphatic compounds.

Examples :



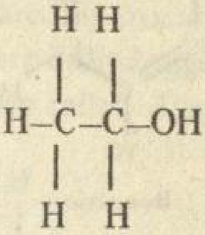
$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array}$$

methane



$$\begin{array}{cccc} & H & H & \\ & | & | & \\ H- & C- & C & -H \\ & | & | & \\ & H & H & \end{array}$$

ethane



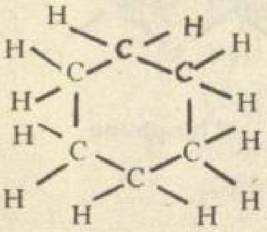
$$\begin{array}{cccc} & H & H & \\ & | & | & \\ H- & C- & C & -OH \\ & | & | & \\ & H & H & \end{array}$$

Ethyl alcohol

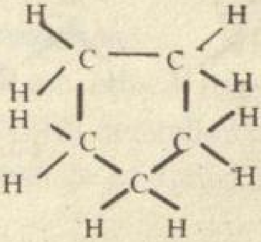
2. **Carbocyclic Compounds** : In carbocyclic compounds the carbon atoms are arranged in rings ; carbocyclic compounds can be further subdivided into following groups :

(*a*) **Alicyclic Compounds** : These cyclic compounds resemble in their properties with aliphatic compounds.

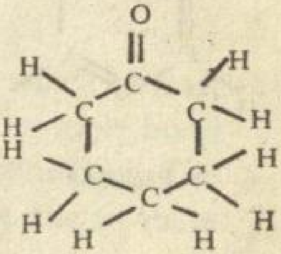
Examples :



Cyclohexane



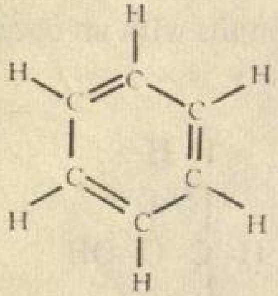
Cyclopentane



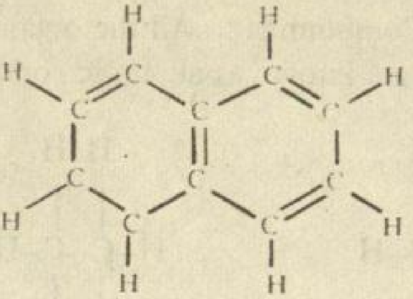
Cyclohexanone

(*b*) **Aromatic Compounds** : Aromatic compounds mainly consist of benzene and its derivatives. Benzene and most of the other aromatic compounds have alternate double bond system. Due to special arrangement of electrons in these compounds their properties are quite characteristic and different from those of aliphatic and alicyclic compounds.

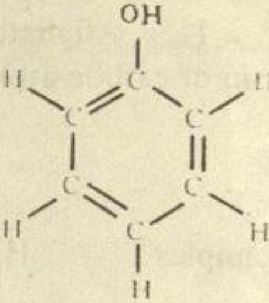
Examples :



Benzene



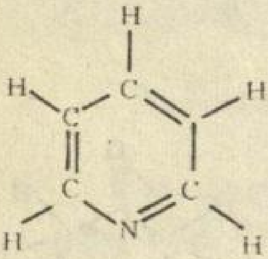
Naphthalene



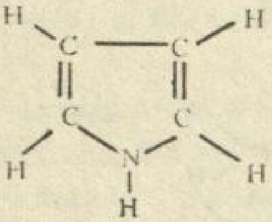
Phenol

3. **Heterocyclic Compounds** : Cyclic Compounds which contain one or more atoms of elements other than carbon as a part of ring are known as heterocyclic compounds. The hetero atoms (other than those of carbon) usually found in heterocyclic compounds are those of nitrogen, oxygen and sulphur.

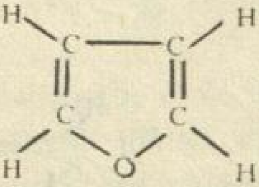
Examples :



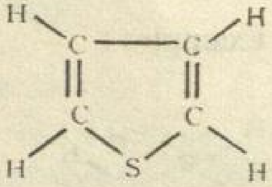
Pyridine



Pyrrol



Furan

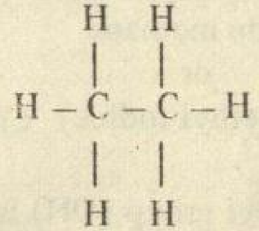


Thiophene

Classification of Organic Compounds on the Basis of Functional Groups : The number of Organic compounds runs into millions. Therefore, it is necessary to systematise the study of Organic Chemistry. To achieve this end the huge number of organic compounds are divided into few classes on the basis of functional groups present in the compounds. Functional group is an atom or group of atoms due to presence of which compound has a characteristic set of properties and some characteristic methods of its preparation. This classification has made the study of Organic Chemistry very systematic and easy. If we can identify a functional group in an organic compound, then we can predict most of its characteristic properties and some methods of its preparation. Thus the study of systematic Organic Chemistry is reached by the study of a few functional groups. Some important classes of organic compounds are described below:-

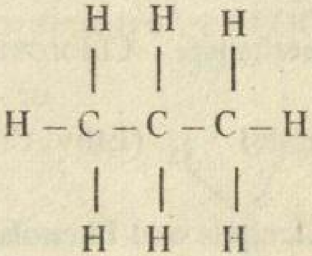
1. **Hydrocarbons :** Compounds having carbon and hydrogen only are called hydrocarbons. Hydrocarbons are further divided into (*a*) saturated hydrocarbons and (*b*) unsaturated hydrocarbons.

(*a*) **Saturated Hydrocarbons or Alkanes :** In saturated hydrocarbons all the carbon atoms present in the molecules are linked together through only single covalent bonds. These are also called alkanes.



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Ethane

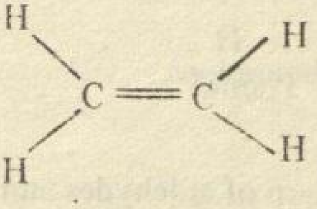


$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

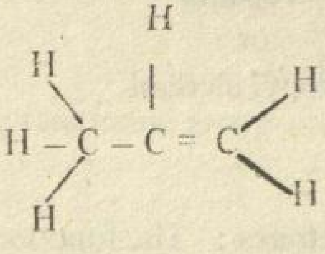
Propane

The group obtained by removing one hydrogen atom from a molecule of hydrocarbon is called alkyl group for example CH_3 from methane (CH_4) and C_2H_5 from ethane (C_2H_6). These alkyl groups are generally represented by R. Thus R represents any hydrocarbon molecule minus one hydrogen atom.

(*b*) **Unsaturated Hydrocarbons :** Hydrocarbons in which at least two carbon atoms are linked together through a multiple bond (double or triple bond) are called unsaturated hydrocarbons. The characteristic properties of these hydrocarbons are due to these multiple bonds.



Ethylene



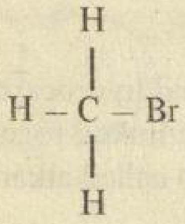
Propylene

$H - C \equiv C - H$ etc.

Acetylene

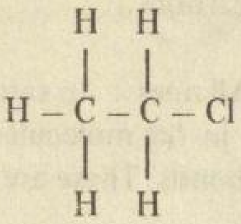
2. **Alkyl halides and Aryl halides :** Alkyl halides (Halo-alkanes) and aryl halides are obtained by replacing one or more hydrogen atoms of an aliphatic hydrocarbon or an aromatic hydrocarbon respectively by halogen atoms. In these compounds halogens are the functional groups due to which

these compounds have the characteristic properties. Alkyl halides are generally represented by R – X (X for halogen).



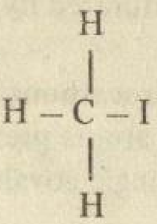
$$\begin{array}{c} H \\ | \\ H-C-Br \\ | \\ H \end{array}$$

Bromomethane
or
(Methyl Bromide)



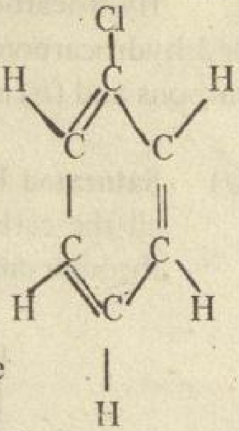
$$\begin{array}{c} H\;\;H \\ |\;\;\;| \\ H-C-C-Cl \\ |\;\;\;| \\ H\;\;H \end{array}$$

Chloroethance
or
(Ethyl Chloride)



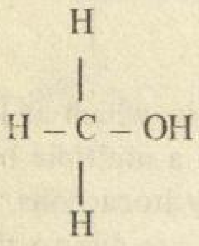
$$\begin{array}{c} H \\ | \\ H-C-I \\ | \\ H \end{array}$$

Iodo methane
or
(Methyl Iodide)



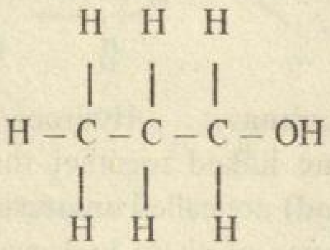
Chlorobenzene

3. **Alcohols and Phenols :** Hydroxyl group (OH) is the functional group of these compounds. Compounds having hydroxyl group attached to aliphatic or alicyclic carbon are called alcohols generally represented by ROH and compounds having hydroxyl group attached to aromatic carbon are called phenols.



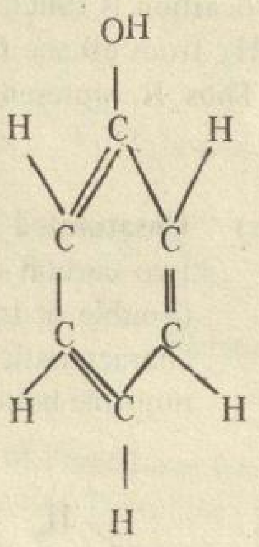
$$\begin{array}{c} H \\ | \\ H-C-OH \\ | \\ H \end{array}$$

Methanol
or
Methyl alcohol



$$\begin{array}{c} H\;\;H\;\;H \\ |\;\;\;|\;\;\;| \\ H-C-C-C-OH \\ |\;\;\;|\;\;\;| \\ H\;\;H\;\;H \end{array}$$

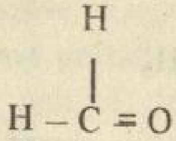
Propanol
or
Propyl alcohol



Phenol

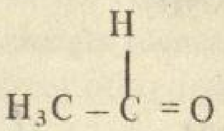
4. **Aldehydes and Ketones :** The functional group of aldehydes and ketones is carbonyl group (C=O). In aldehydes carbonyl carbon is attached with one or two hydrogen atoms and in ketones carbonyl carbon is attached with two carbon atoms.

Aldehydes and ketones are generally represented by R – CHO and $R-\overset{\overset{O}{\|}}{C}-R$ respectively.



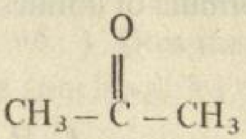
$$H-\overset{H}{\overset{|}{C}}=O$$

Formaldehyde



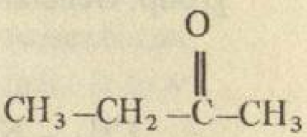
$$H_3C-\overset{H}{\overset{|}{C}}=O$$

Acetaldehyde



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

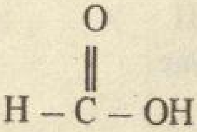
Dimethyl Ketone



$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

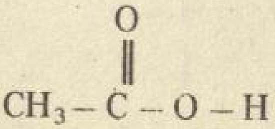
Ethylmethyl Ketone

5. **Carboxylic Acids** : Carboxyl group ($-\overset{O}{\overset{\|}{C}}-OH$) is the functional group of carboxylic acids. These are generally represented by RCOOH.



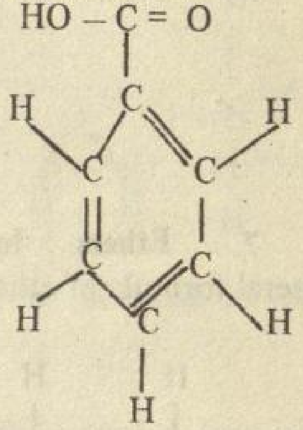
$$H-\overset{O}{\overset{\|}{C}}-OH$$

Formic acid



$$CH_3-\overset{O}{\overset{\|}{C}}-O-H$$

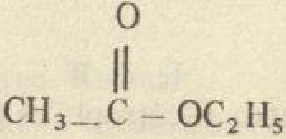
Acetic acid



Benzoic acid

Some important derivatives of acids are as below :

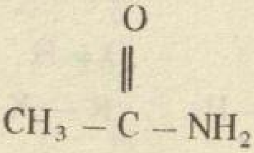
(*i*) Esters with functional group $-\overset{O}{\overset{\|}{C}}-OR$ *e.g.*,



$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5$$

Ethyl acetate

(*ii*) Amides with the functional group $-\overset{O}{\overset{\|}{C}}-NH_2$ *e. g.*,

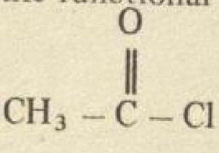


$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2$$

Acetamide

(*iii*) Acid halides with the functional group $-\overset{O}{\overset{\|}{C}}-X$

e. g.,



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl$$

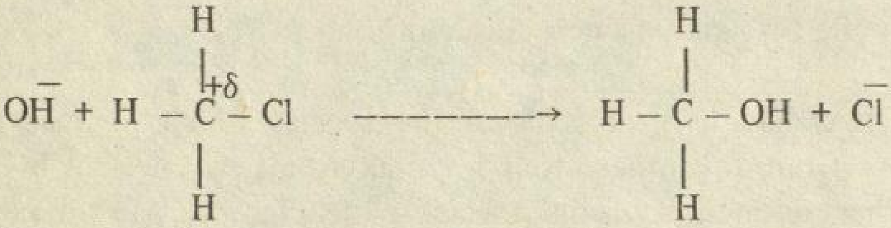
Acetyl chloride

Free radicals are usually very much reactive and unstable. The two free radicals either same or different combine together readily forming a new covalent bond.

Important Types of Organic Reactions:

1. **Substitution Reactions.** These reactions are the characteristic reactions of saturated organic compounds. These reactions involve the replacement of atom or group by some other atom or group. The substance in which substitution takes place is called substrate, while replacing atom or group is called substituent or entering group and the group to be replaced is termed as leaving group. On the basis of the nature of substituent, substitution reactions may be sub-divided into two types :

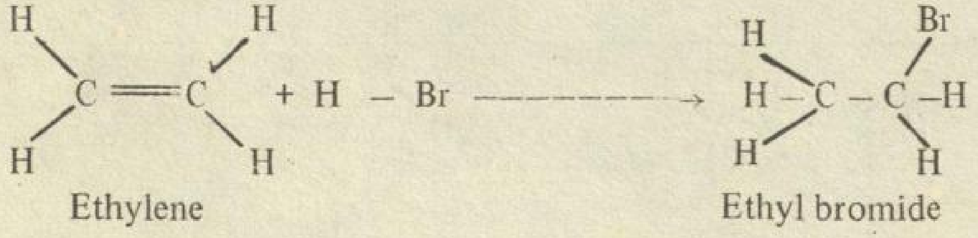
(*i*) **Nucleophilic Substitution**, if the substituent is a nucleophile.



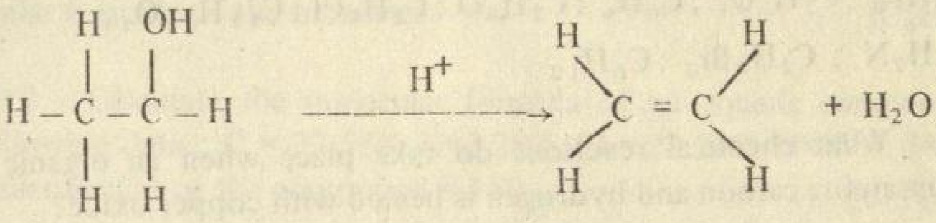
$$\overset{-}{OH} + H - \begin{array}{c} H \\ | \\ \overset{+\delta}{C} \\ | \\ H \end{array} - Cl \xrightarrow{\qquad} H - \begin{array}{c} H \\ | \\ C \\ | \\ H \end{array} - OH + \overset{-}{Cl}$$

(*ii*) **Electrophilic Substitution**, if the substituent is an electrophile.

2. **Addition Reactions.** These reactions take place in the compounds containing multiple bonds either between carbon atoms or between carbon and oxygen or between carbon and nitrogen. If the adding species is a nucleophile the addition will be nucleophilic and if the adding species is electrophile, it will be electrophilic addition. Addition to carbon-carbon multiple bond is usually electrophilic while addition to carbon-oxygen double bond is usually nucleophilic.

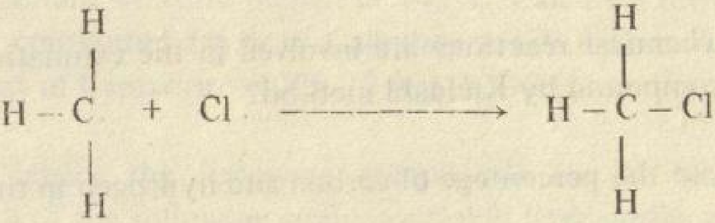


3. **Elimination Reactions.** In these reactions two groups or atoms are eliminated from the two adjacent carbon atoms forming a multiple bond between these two carbon atoms.



Ethyl alcohol Ethylene

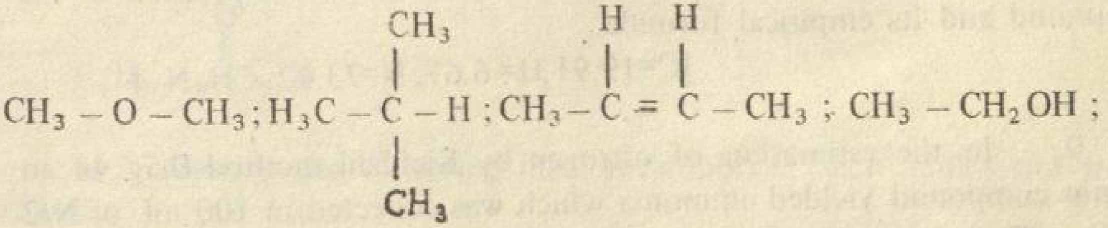
4. **Free Radical Reactions.** These reactions involve formation of covalent bond between two free radicals. These reactions generally take place in the presence of light and in nonpolar solvents.



$$H_3C\cdot + Cl\cdot \longrightarrow H_3C-Cl$$

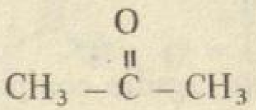
QUESTIONS

1. Why is it necessary to know the structure of an organic compound? Why is isomerism very common in Organic Chemistry ? Which of the following compounds are isomers ?



CH_3-O-CH_3 ; $H_3C-\overset{CH_3}{\underset{CH_3}{C}}-H$; $CH_3-\overset{H}{C}=\overset{H}{C}-CH_3$; CH_3-CH_2OH ;

$CH_2=CH-CH_2OH$; $CH_2=CH-CH=CH_2$; $CH_3-CH_2-CH_2-CH_3$



$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

2. Explain the following terms :

Structural formula, molecular formula and empirical formula. Some of the organic compounds have the following molecular formulae, write their empirical formula :

C_4H_{10} ; $C_2H_2O_4$; C_6H_6 ; C_2H_6O ; C_2H_5Cl ; $C_{11}H_{22}O_{11}$;
C_2H_7N ; $C_2H_4Br_2$; C_6H_{12} .

3. What chemical reactions do take place when an organic compound containing carbon and hydrogen is heated with copper oxide?

4. What will be the products when an organic compound of molecular formula $C_5H_4BrNSO_3$ is fused with metallic sodium ?

5. Give the outlines of the methods for estimating carbon and hydrogen in an organic compound.

6. What chemical reactions are involved in the estimation of nitrogen in an organic compound by Kjeldahl method?

7. Calculate the percentage of carbon and hydrogen in the following compounds ?

(a) 0.1915 g. of a compound gave 0.3059 g. of CO_2 and 0.0657 g. H_2O. [C=43.55, H=3.81]

(b) 0.0151 g. of a compound gave 0.0105 g. of CO_2 and 0.0068 g. of H_2O. [C=18.96,H=5.00]

8. 0.1 g. of an organic compound containing C, H and N gave 0.073 g. CO_2 and 0.06 g. of H_2O. Calculate the percentage composition of the compound and its empirical formula.

[C=19.91,H=6.67, N=73.42, CH_4N_3]

9. In the estimation of nitrogen by Kjeldahl method 0.5g. of an organic compound yielded ammonia which was collected in 100 ml. of N/2 H_2SO_4. The excess of sulphuric acid required 67.2 ml. of N/2 NaOH for neutralization. Calculate the percentage of nitrogen. [45.92 %]

10. Calculate the molecular formula of an organic compound from the following data.

0.1023 g. of the compound gave 0.1492 g. of CO_2 and 0.0627 g. of H_2O. Mol. Wt. of the compound is 60. [$C_2H_4O_2$]

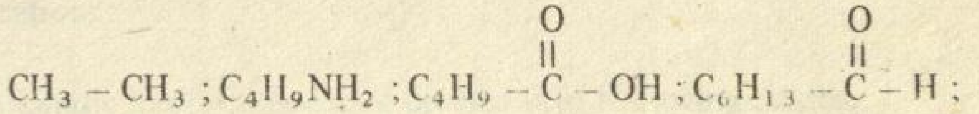
11. 0.1 g. of a substance gave 0.2002 g. of CO_2 and 0.081 g. of H_2O. 0.1 g. of the substance displaced 27.0 ml. of air measured at 15°C and 745 mm. pressure. (Vapour tension at 15°C = 12.7 mm). Calculate the molecular formula of the substance. [$C_4H_8O_2$]

12. Calculate the molecular formula of an organic compound from the following data : C = 23.58%, H=3.28%, Cl = 23.23%, N=18.4. S=21.00%, molecular weight of the compound = 150. [$C_3H_5ClN_2SO$]

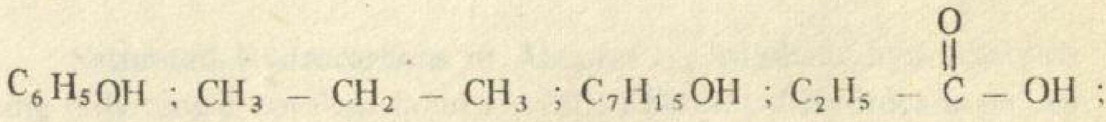
13. Why only camphor is used in Rast's method for the determination of molecular weight of an organic compound ? What are the limitations of this method ?

3.088g. of camphor was mixed with 0.298 g. of an organic compound. The resultant mixture melted at 147°C. Calculate the molecular weight of the compound (m.p. of Camphor = 176.0°C, molecular depression constant of Camphor = 400). [Ans. 133.1].

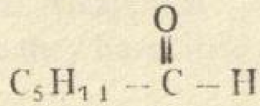
14. Classify the following compounds on the basis of functional groups. Which of the following compounds will have similar properties ?



$CH_3-CH_3\ ;C_4H_9NH_2\ ;C_4H_9-\overset{\overset{O}{\|}}{C}-OH\ ;C_6H_{13}-\overset{\overset{O}{\|}}{C}-H\ ;$



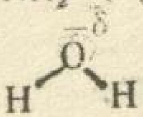
$C_6H_5OH\ ;\ CH_3-CH_2-CH_3\ ;\ C_7H_{15}OH\ ;\ C_2H_5-\overset{\overset{O}{\|}}{C}-OH\ ;$



$C_5H_{11}-\overset{\overset{O}{\|}}{C}-H$

15. Classify the following into nucleophiles, electrophiles and free radicals.

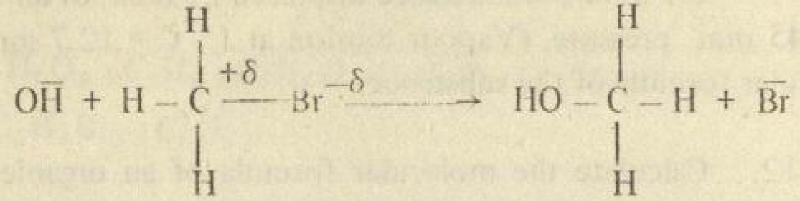
$\overline{N}H_2\ ;\ (C_6H_5)_3\overset{-}{C}\ ;\ N\overset{+}{O}\ ;\ \overset{+}{H},\ R-\overset{..}{N}H_2\ ;\ (CH_3)_3\overset{+}{C}\ ;\ \dot{C}_6H_5$



$;\ O=\overset{+\delta}{C}=O\ ,\ SO_3\ ;\ CH_3\ ;$

16. Classify the following reactions:

(*i*)



$$\overset{-}{OH} + H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}\overset{+\delta}{}\!-\!\!-Br^{-\delta} \longrightarrow HO-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H + \overset{-}{Br}$$

(*ii*) $CH_3 - \dot{C}H_2 + \dot{C}l \longrightarrow CH_3 - CH_2 - Cl$

(*iii*) $H_2C = CH_2 + H - Br \longrightarrow CH_3 - \overset{+}{C}H_2 \xrightarrow{Br^-}$ $CH_3 - CH_2 - Br$

(*iv*) $H_3C - CH_2 - Br \longrightarrow H_2C = CH_2 + H - Br$

CHAPTER 14

ALIPHATIC HYDROCARBONS

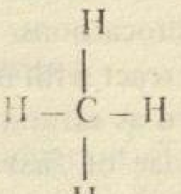
Open chain compounds containing only carbon and hydrogen are called Aliphatic Hydrocarbons. By substituting hydrogen atoms of the hydrocarbon by other atoms or groups a large number of organic compounds can be obtained Therefore, hydrocarbons are considered to be the parent compounds of all other organic compounds.

Classifications:

Aliphatic hydrocarbons are divided into following classes:

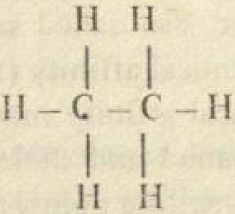
1. **Saturated Hydrocarbons or Alkanes :** Aliphatic hydrocarbons containing only single covalent bond are called Saturated Hydrocarbons or Alkanes. Alkanes are also called paraffins (para = little, affins = affinity) because they have little affinity for reaction with other substances.

Examples:



$$\begin{array}{ccc} & H & \\ & | & \\ H - & C & - H \\ & | & \\ & H & \end{array}$$

Methane



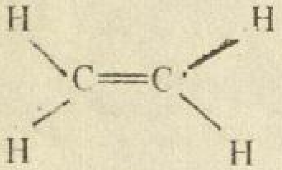
$$\begin{array}{cccc} & H & H & \\ & | & | & \\ H - & C - & C & - H \\ & | & | & \\ & H & H & \end{array}$$

Ethane

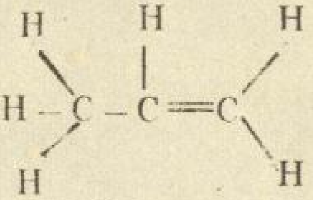
2. **Unsaturated Hydrocarbons.** Unsaturated hydrocarbons have one or more than one multiple bonds between carbon atoms. These are further sub-divided into following sub-classes:

(*a*) **Olefines or Alkenes :**

Alkenes have one double bond between carbon atoms e.g., ethene, propene etc.



Ethene



Propene

(*b*) **Alkynes or Acetylenes :**

Unsaturated hydrocarbons containing one triple bond between carbon atoms are called alkynes or acetylenes *e.g.*, acetylene, propyne.

$H - C \equiv C - H$ — Acetylene

$CH_3 - C \equiv C - H$ — Propyne

ALKANES :

The general formula of alkanes is C_nH_{2n+2} where n is the number of carbons in the molecule of alkane. For example, an alkane having five carbons in its molecule, will have twelve hydrogens in its molecule with the formula C_5H_{12}. Alkanes have maximum number of hydrogen atoms and no more hydrogen or any other atom or group can be added to their molecules. Therefore, alkanes are also called saturated hydrocarbons. Moreover, since alkanes have little chemical affinity (tendency to react with other substances) therefore, their chemical affinity may be regarded as saturated and satisfied. In table 14. 1 the names and molecular formulae of first ten alkanes are given along with their melting points and boiling points.

TABLE 14.1

Name	Formula	M.P.°C	B.P.°C
Methane	CH_4	−183	−162
Ethane	C_2H_6	−172	− 88.5
Propane	C_3H_8	−187	− 42
Butane	C_4H_{10}	− 138	0
Pentane	C_5H_{12}	−130	36
Hexane	C_6H_{14}	− 95	69
Heptane	C_7H_{16}	− 90.5	98
Octane	C_8H_{18}	− 57	126
Nonane	C_9H_{20}	− 54	151
Decane	$C_{10}H_{22}$	− 30	174

Homologous Series :

The examination of molecular formulae of the alkanes given in Table 14.1 reveals that each hydrocarbon has one carbon and two hydrogens less than the next higher hydrocarbon. For example ethane (C_2H_6) has one – CH_2– (methylene group) less than propane (C_3H_8) and propane has one –CH_2 – group less than butane (C_4H_{10}). A series of compounds in which all members have similar structural features but each member differing from the next member by one methylene group (–CH_2), is called a homologous series. The members of a homologous series are called homologues. Thus the alkanes form a homologous series. All the members of a homologous series have similar chemical properties and show gradual change in their physical properties like m.p., b.p. etc. with the increasing molecular weights. A knowledge of the properties of one member of the series enable us to predict the properties of the other member of that homologous series. Methods of preparation of the members of a homologous series are also similar.

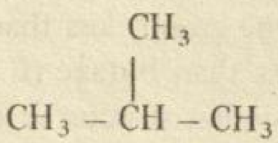
Alkyl groups. The group obtained by subtracting one hydrogen from the molecule of an alkane, is called an alkyl group. Alkyl group is generally represented by R. The name of alkyl group is derived by replacing – *ane* from the name of the parent alkane by – *yl.* For example methyl ($-CH_3$) from methane, ethyl ($-C_2H_5$) from ethane, propyl ($-C_3H_7$) from propane etc.

Nomenclature. It has been mentioned earlier that there are more than one million of organic compounds and it is impossible to memorise the names of all the individual organic compounds. Therefore, it was necessary to devise some systematic method for naming the organic compounds. Several such methods for naming the organic compounds were devised. The most systematic method is that adopted by the International Union of Pure and Applied Chemistry (IUPAC) and generally referred as IUPAC system. All the other modes of nomenclature are called common system. In some cases, specially in simple molecules, the names of common system are simple and easy to remember as compared to the names of IUPAC system. Therefore, for simple compounds their common names are frequently used. The IUPAC system is especially useful for naming the large and complex molecules.

Common System. The first four alkanes are named as methane, ethane, propane and butane . The names of the remaining alkanes are derived from Greek prefix for the number of carbons in the alkane and suffix – *ane* is added. For example alkane with five carbons is called pentane (penta = five) and the alkane with six carbons is named as hexane (hexa = six) Alkanes having four or more carbons have several isomers depending upon the ways in which carbons are linked together. For example, four carbons of butane can be arranged in two ways and five carbons of pentane can be arranged in three different ways.

$H_3C - CH_2 - CH_2 - CH_3$

n – Butane



$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C}H - CH_3$$

isobutane

IUPAC System. The parent names of alkanes (given in Table 14.1) are retained in this system but different rules have been devised for naming the other isomers. Each branched hydrocarbon is considered to be alkyl derivative of the alkane with longest continuous chain of carbons. The rules for naming the branched alkanes are given below :-

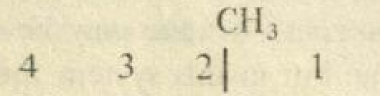
1. The longest continuous chain of carbons is selected and the compound is considered to be the derivative of this parent hydrocarbon.

2. Carbons of continuous chain are numbered. Numbering starts from the end which gives the smallest value to the carbons carrying the substituents (substituent is an atom or group of atoms other than hydrogen) attached to carbon, in case of alkanes the substituent is an alkyl group.

3. Substituents are named before the name of the parent hydrocarbon and the positions of substituents are indicated by putting before their names the numbers of carbons to which the respective substituents are attached. If the same substituent is present more than once in the molecule, its number is indicated by the prefix di – (for two), tri – (for three), tetra – (for four) and so on.

4. If there are more than one kind of substituents, they are generally named in the alphabetical order.

These rules are explained by the following examples :

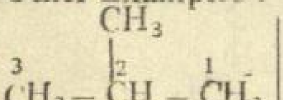


$$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{\overset{CH_3}{2|}}{CH}-\overset{1}{CH_3}$$

2-methyl butane

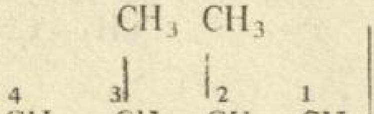
In the above example the longest continuous chain has four carbons, therefore, the hydrocarbon is butane. Numbering of carbons of the continuous chain starts from the right end to give the smallest possible number to carbon having methyl group.

Other Examples :



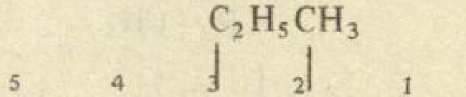
$$\overset{3}{CH_3}-\overset{\overset{CH_3}{|2}}{CH}-\overset{1}{CH_3}$$

2-Methylpropane



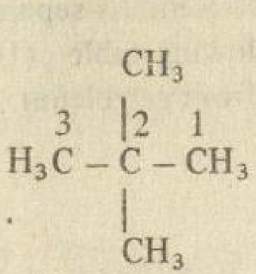
$$\overset{4}{CH_3}-\overset{\overset{CH_3}{3|}}{CH}-\overset{\overset{CH_3}{|2}}{CH}-\overset{1}{CH_3}$$

2,3–Dimethylbutane

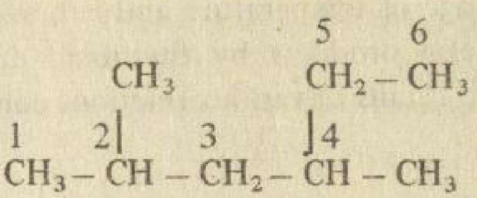


$$\overset{5}{CH_3}-\overset{4}{CH_2}-\overset{\overset{C_2H_5}{3|}}{CH}-\overset{\overset{CH_3}{2|}}{CH}-\overset{1}{CH_3}$$

3 – Ethyl-2-methylpentane



$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

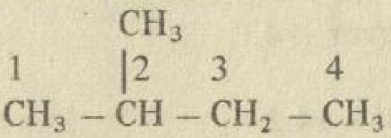


$$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_2-CH_3}{|}}{CH}-CH_3$$

2, 2– Dimethyl propane 2, 4 – Dimethylhexane.

Primary, Secondary and Tertiary Carbons and Hydrogens :

A carbon attached to only one other carbon in the molecule is called primary carbon. Hydrogens attached to primary carbons are called primary hydrogens. The carbon attached to two other carbons is called secondary carbon and hydrogens attached to the secondary carbons are called secondary hydrogens. A carbon attached to three carbons is called tertiary carbon and hydrogens attached to the tertiary carbons are called tertiary hydrogens.



$$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_3$$

In the above example C_1 and C_4 are primary carbons, C_3 is secondary carbon and C_2 is tertiary carbon.

Natural Sources of Alkanes : Alkanes are distributed in nature in large quantities. Petroleum and Natural gas are important sources of alkanes.

Petroleum. Huge deposits of petroleum are found under the earth's crust in certain parts of the world. Petroleum (petra-rock, oleum-oil) or crude oil is an oily liquid. The important petroleum producing countries are U.S.A. Venezuela, Iran Iraq and other Middle East Countries. Pakistan has also some deposits of petroleum in Chakwal district of the Punjab Province. Petroleum usually occus at moderate depths, sometimes 5,000 feet or more under earth's crust. The oil is found in porous strata beneath the impervious rock. It is obtained by drilling a hole in the earth's crust down which iron pipes are lowered.

Refining of Petroleum. The crude petroleum is a dark brown viscous liquid often having an offensive odour. It consists of alkanes boiling in the wide range of temperature and is never used as such. Petroleum is separated into useful products by fractional distilation. The following table (14.2) gives the details of various fractions commonly obtained from petroleum.

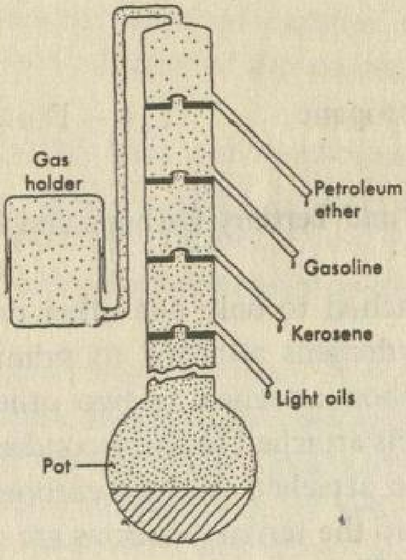


Diagram 14.1

TABLE 14.2

Name of Fraction.	Boiling Range °C	Composition	Uses
1. Gases	Below 20°C	$C_1 - C_4$	Fuel Gas
2. Gasoline	40 – 200	$C_5 - C_{10}$	
Refractionated to yield			
(i) Petroleum ether	40 – 80		Solvent
(ii) Gasoline or petrol	80 – 200		Motor Fuel, solvent and for dry cleaning.
3. Kerosene oil	200 – 300	$C_{11} - C_{16}$	Illuminant, Fuel for stoves and for making oil gas

4.	Gas oil or Fuel oil.	Above 300	$C_{10} - C_{18}$	Fuel for diesel engines, for conversion to gasoline by cracking.
5.	Residual oil. Refractionated under vacuum to give.			
(i)	Lubricant		$C_{17} - C_{20}$	Lubrication
(ii)	Paraffin Wax		$C_{20} - C_{30}$	Ointments, Candles,Toilets, Vaseline and Waxpaper.
(iii)	Residue (Asphalt and Pitch).			Paints and Road - surfacing).

Oil refineries in Pakistan are located at Rawalpindi and Karachi.

Natural Gas

It is the term applied to the large quantities of gas associated with or unassociated with liquid petroleum. The composition of the natural gas varies with the source and consists of chiefly the first four paraffins. The percentage of the hydrogen decreases with increasing molecular weight.

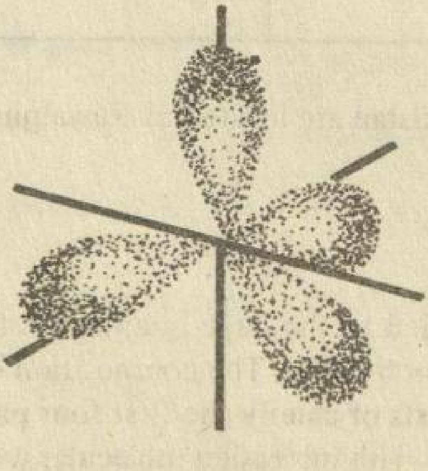
The percentage of methane is generally from 70 – 85%. Other gases such as water vapours, nitrogen, carbon dioxide and hydrogen sulphide may be present in small amounts. Pakistan has huge deposits of natural gas at Sui (Baluchistan). This gas is being exploited for industrial and domestic uses.

Electric power plants and various factories use this gas as fuel. Chemical fertilizers are also being prepared from the Sui gas. The supply of Sui gas has been extended to Peshawar, Nowshera and Mardan in N.W.F.P. The composition of Sui gas is given below :

Methane	Ethane	Propane	Butane	N_2	CO_2
88.52 %	0.89	0.26	0.37	2.46	7.35

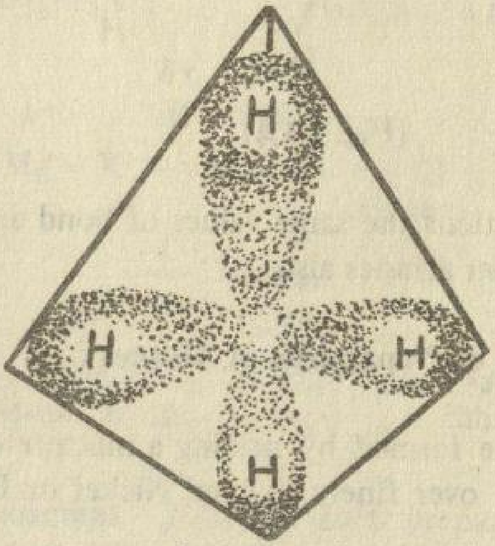
Structure of Alkanes :

In each carbon atom of alkanes one 2s orbital and three 2p orbitals mix together forming four new equivalent hybridised orbitals. These four hybridised orbitals are directed to the four corners of a regular tetrahedron and are called Sp^3 orbitals. There is an angle of 109.5° between any two hybridised orbitals. Tetrahedral structure permits the hybridised orbitals to be as far apart from each other as possible.



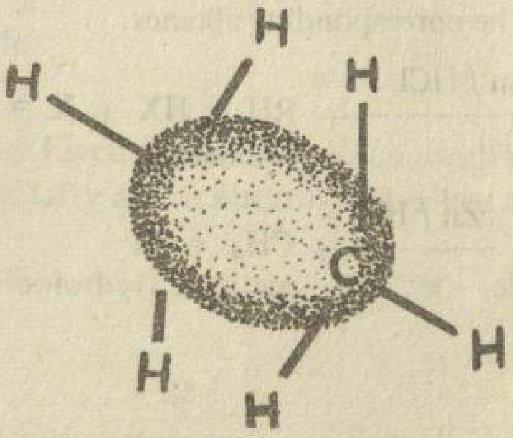
Sp^3 orbitals
(Fig. 14.3)

In case of methane each of the four Sp^3 orbitals of carbon overlap with spherical S orbitals of four hydrogen atoms forming four covalent bonds. For effective overlapping the four S orbitals of four hydrogens should be at the four corners of the tetrahedron. In these covalent bonds the electronic density of the shared pair of electrons is cylindrically symmetrical about the line joining the two nuclei. Therefore, these covalent bonds are called σ (sigma) bonds. Thus in methane the four hydrogen atoms are located at the four corners of a regular tetrahedron with carbon at the centre of the tetrahedron. The angle between any two bonds is 109.5° and C – H bond length is 1.09A°

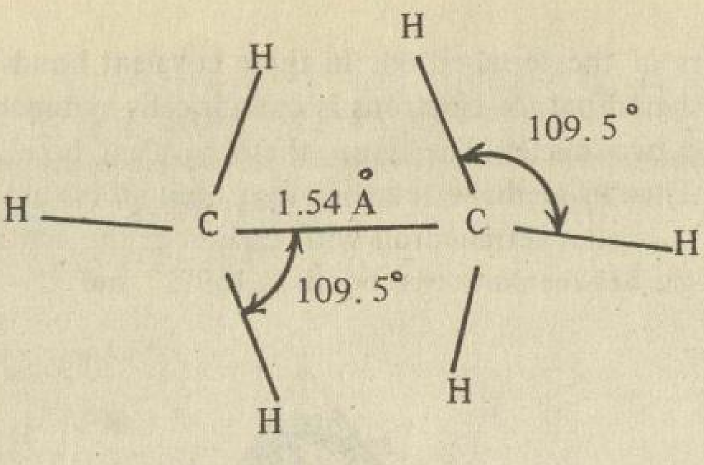


One tetrahedral methane molecule
(Fig. 14.4)

Each of the two carbons of ethane also has four [Sp^3] hybridised orbitals directed towards the four corners of a regular tetrahedron. Three of the four hybridised orbitals of each carbon overlap with S orbitals of three hydrogens, thus, forming six C – H sigma bonds. The remaining fourth hybridised orbital on each carbon overlap with each other forming another sigma bond between two carbons. In this case also bond angle between any two bonds is 109.5° . C – H bond length is 1.10A° and C – C bond length is 1.54A°.



Molecule of Ethane
(Fig.14. 5)



(Fig. 14.4)

With slight variations the same values of bond angles and bond length have been found in other alkanes also.

General Methods of Preparation of Alkanes :

1. Alkanes are formed by passing a mixture of unsaturated hydrocarbons and hydrogen over finely divided Nickel or Platinum or palladium at 250°C to 300°C

$$\underset{\text{Alkene}}{C_nH_{2n}} + H_2 \xrightarrow[250-300^\circ C]{\text{Ni or Pt or Pd}} \underset{\text{Alkane}}{C_nH_{2n+2}}$$

$$\underset{\substack{\text{ethene or}\\ \text{ethylene}}}{CH_2 = CH_2} + H_2 \xrightarrow[\text{Ni or Pt } (250-300^\circ C)]{} \underset{\text{Ethane}}{CH_3 - CH_3}$$

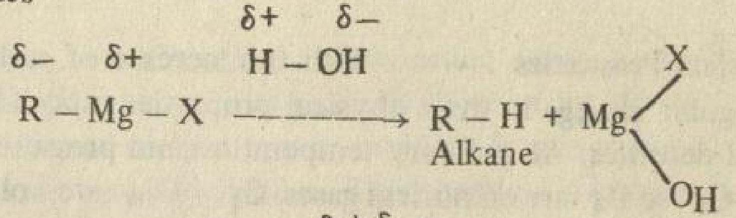
Reduction of Alkyl Halides. When reduced by metal and acid, alkyl halides are converted to the corresponding alkanes.

$$\underset{\text{Alkyl Halide}}{RX} + 2H \xrightarrow{Zn / HCl} \underset{\text{Alkane}}{RH} + HX \quad (X = \text{a halogen atom})$$

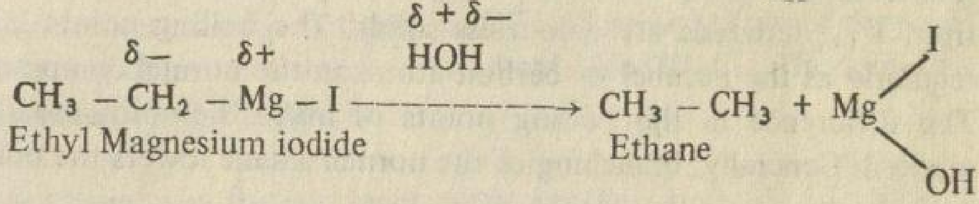
$$\underset{\text{methyl Iodide}}{CH_3I} + 2H \xrightarrow{Zn / HCl} \underset{\text{methane}}{CH_4} + \underset{\text{Hydroiodic acid}}{HI}$$

3. **By Hydrolysis of Grignard's reagent.** Alkyl halides react with magnesium in presence of ether to give alkyl magnesium halides known as Grignard's reagent which on hydrolysis with water give alkanes.

$$\underset{\text{Alkyl halides}}{RX} + \underset{\text{Magnesium}}{Mg} \xrightarrow{\text{Ether}} \underset{\text{Grignard's reagents}}{R-Mg-X}$$



$$\overset{\delta- \quad \delta+}{R-Mg}-X + \overset{\delta+ \quad \delta-}{H-OH} \longrightarrow \underset{\text{Alkane}}{R-H} + Mg\begin{smallmatrix} X \\ OH \end{smallmatrix}$$



$$\underset{\text{Ethyl Magnesium iodide}}{\overset{\delta- \qquad \delta+}{CH_3-CH_2-Mg}-I} + \overset{\delta+\delta-}{HOH} \longrightarrow \underset{\text{Ethane}}{CH_3-CH_3} + Mg\begin{smallmatrix} I \\ OH \end{smallmatrix}$$

4. **By Wurtz reaction.** In 1885 Wurtz prepared alkanes by treating an ethereal solution of an Alkyl halide (preferably the bromide or iodide) with sodium metal.

$$R-X + 2Na \longrightarrow \underset{\text{Alkane}}{R-R} + 2NaX$$

$$+$$

$$\underset{\text{Alkyl halide}}{R-X}$$

$$CH_3-Br + 2Na \longrightarrow \underset{\text{Ethane}}{CH_3-CH_3} + 2NaBr$$

$$+$$

$$\underset{\text{methyl bromide}}{CH_3-Br}$$

5. **By Kolbe Electrolysis.** When concentrated solution of sodium or potassium salt of a fatty acid is electrolysed, a higher alkane is obtained

$$2\,RCOOK \longrightarrow 2\,RCO\overset{-}{O} + 2\overset{+}{K}$$

At anode

$$2\,RCO\overset{-}{O} \xrightarrow{-2e} 2R + 2CO_2;\ 2R \longrightarrow \underset{\text{alkane}}{R-R}$$

At Cathode

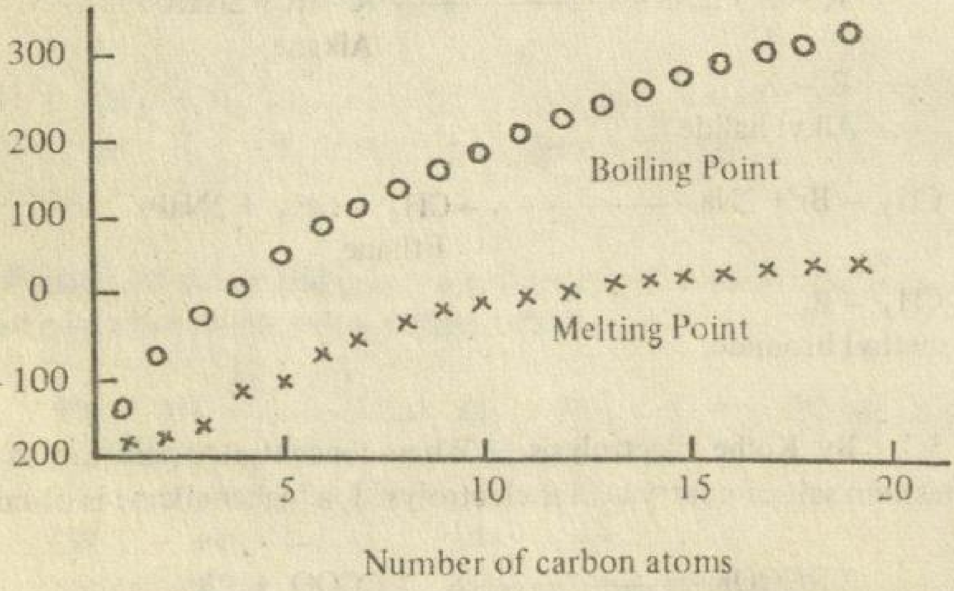
$$2\overset{+}{K} \xrightarrow{+2e} 2K$$

$$2K + 2H_2O \longrightarrow 2KOH + H_2$$

GENERAL PROPERTIES OF ALKANES

Physical Properties : - With the increase of carbon atoms alkanes show a regular change in their physical properties especially in their boiling points and densities. At ordinary temperature and pressure the normal paraffins from C_1 to C_4 are colourless gases. $C_5 - C_{17}$ are colourless liquids and from C_{18} onwards are colourless solids. The boiling points increase fairly regularly as the number of carbon atoms in the normal compound increases. The difference in the boiling points of higher homologues is not so well marked. Generally, branching of the normal alkane lowers the boiling point.

When the boiling points are plotted against the number of carbon atoms they follow a smooth curve as shown below:-

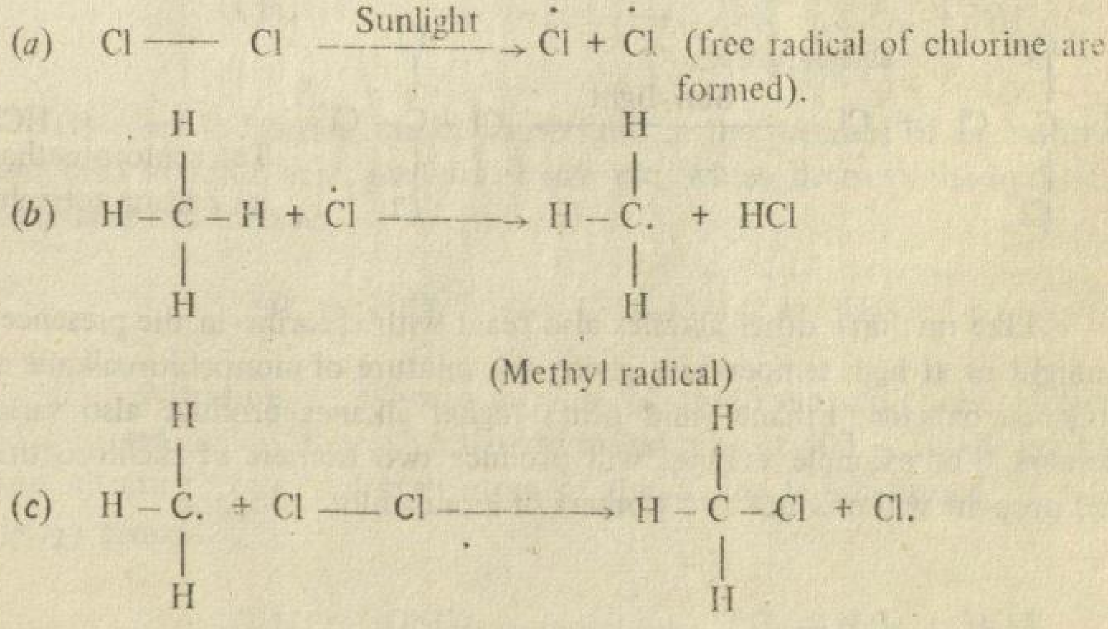


Other Physical properties such as melting points, specific gravity viscosity also increase with increasing carbons in the molecule.

Chemical Properties : - Alkanes have no functional groups and are characterised by their stability and chemical inertness. Under ordinary conditions and at room temperature alkanes do not react with aqueous acids, alkalies, oxidising agents and reducing agents. Thus the chemical affinity of an alkane may be regarded as saturated and satisfied. However, at elevated temperatures alkanes are oxidised by oxygen into carbon dioxide and water. Alkanes also give some substitution reactions for example with chlorine and nitric acid under specified conditions.

Halogenation : - Chlorine and bromine react with alkanes with considerable ease in the presence of sunlight, heat or by the use of catalyst like iron filings. Halogens replace one or more hydrogen atoms of the alkane producing haloalkanes or alkyl halides. This reaction is known as halogenation. Thus chlorine reacts with methane in diffused sunlight (photo chemical reaction) producing chloromethane or methyl chloride CH_3Cl . Thus chlorine has been substituted for hydrogen.

Chloromethane can further react with another molecule of chlorine forming dichloromethane or methylene chloride, CH_2Cl_2. Further chlorination may produce trichloromethane or chloroform. $CHCl_3$ and tetrachloromethane or carbon tetrachloride. Thus in this reaction usually the mixture of all these four products is obtained. Therefore, this method is not suitable for laboratory preparation of alkyl halides. The following steps are involved in the chlorination of methane.



(*a*) $Cl - Cl \xrightarrow{\text{Sunlight}} \dot{Cl} + \dot{Cl}$ (free radical of chlorine are formed).

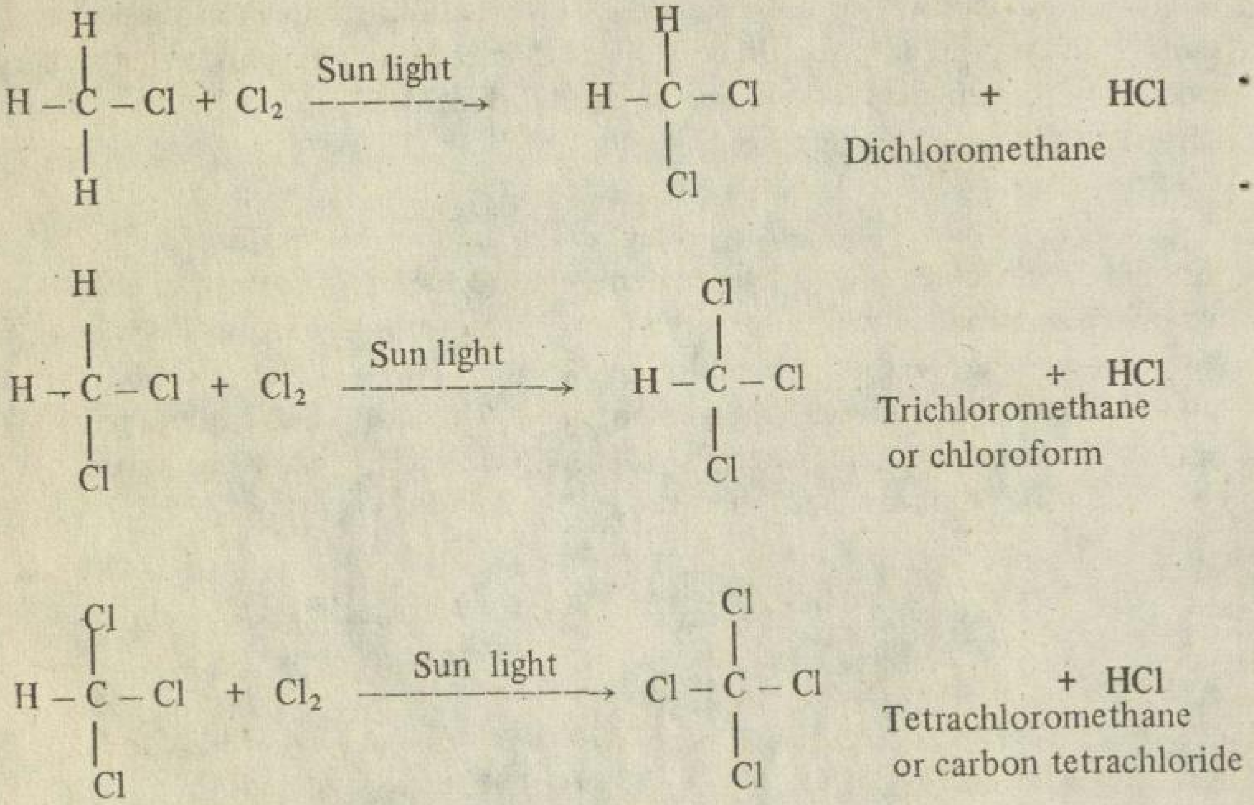
(*b*) $H-\overset{H}{\underset{H}{C}}-H + \dot{Cl} \longrightarrow H-\overset{H}{\underset{H}{C}}. + HCl$

(Methyl radical)

(c) $H-\overset{H}{\underset{H}{C}}. + Cl - Cl \longrightarrow H-\overset{H}{\underset{H}{C}}-Cl + Cl.$

Thus we see that the chlorination of methane proceeds through the formation of free radicals. The Cl atom formed in step (c) can react with another molecule of methane and thus a chain reaction sets in. The first step in this reaction is known as chain initiating step, the second and third steps are called chain propagating steps.

The detailed step by step description of a chemical reaction is called the mechanism of the reaction. Therefore the above step-wise description of chlorination of methane is the mechanism of this reaction. The knowledge of mechanism of a chemical reaction is very important and useful in organic chemistry.



$$H-\overset{H}{\underset{H}{C}}-Cl + Cl_2 \xrightarrow{\text{Sun light}} H-\overset{H}{\underset{Cl}{C}}-Cl + HCl$$

Dichloromethane

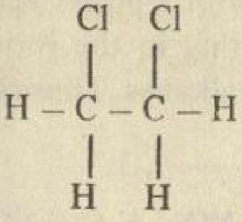
$$H-\overset{H}{\underset{Cl}{C}}-Cl + Cl_2 \xrightarrow{\text{Sun light}} H-\overset{Cl}{\underset{Cl}{C}}-Cl + HCl$$

Trichloromethane
or chloroform

$$H-\overset{Cl}{\underset{Cl}{C}}-Cl + Cl_2 \xrightarrow{\text{Sun light}} Cl-\overset{Cl}{\underset{Cl}{C}}-Cl + HCl$$

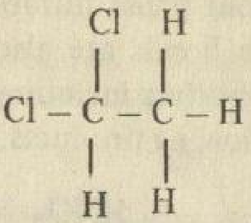
Tetrachloromethane
or carbon tetrachloride

Like methane other alkanes also react with chlorine in the presence of sunlight or at high temperature giving the mixture of monochloroalkane and polychloroalkane. Ethane and other higher alkanes produce also various isomers. For example ethane will produce two isomers of dichloroethane and propane will produce two isomers of mono-chloro-propane.



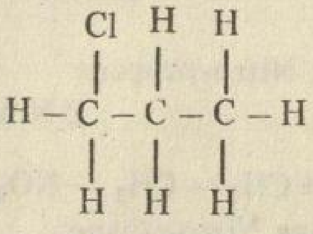
$$\begin{array}{ccccccc} & & \mathrm{Cl} & & \mathrm{Cl} & & \\ & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

1, 2 – Dichloroethane



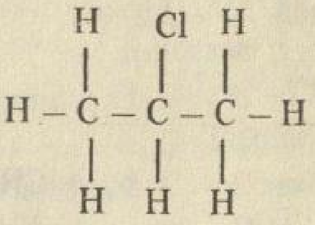
$$\begin{array}{ccccccc} & & \mathrm{Cl} & & \mathrm{H} & & \\ & & | & & | & & \\ \mathrm{Cl} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

1, 1 – Dichloroethane



$$\begin{array}{ccccccccc} & & \mathrm{Cl} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

1 – Chloropropane



$$\begin{array}{ccccccccc} & & \mathrm{H} & & \mathrm{Cl} & & \mathrm{H} & & \\ & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

2 – Chloropropane

The mechanism of chlorination of higher alkanes is similar to that of methane.

Fluorine reacts explosively, bromine reacts less vigorously than chlorine. Iodine does not react with alkanes as the HI produced during iodination, reduces the alkyl halides back to the hydrocarbon.

$$\mathrm{CH_4} + \mathrm{I_2} \longrightarrow \underset{\text{methyl iodide}}{\mathrm{CH_3I}} + \mathrm{HI}$$

However iodination can be carried out in the presence of an oxidising agent such as iodic acid, mercuric oxide etc, which destroys the hydro-iodic-acid (HI) as it is formed.

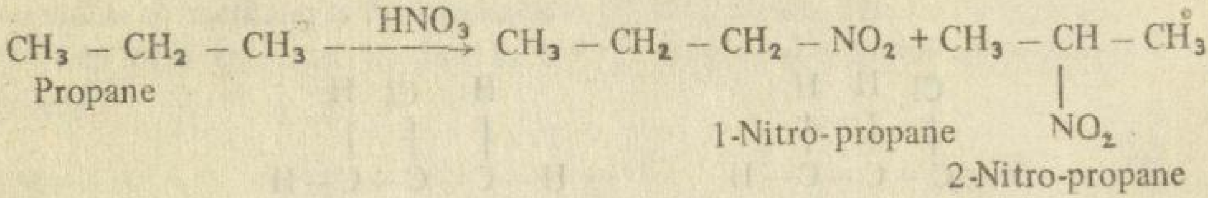
$$5\mathrm{HI} + \mathrm{HIO_3} \longrightarrow 3\mathrm{I_2} + 3\mathrm{H_2O}$$

(*i*) **Nitration** : When a mixture of an alkane and excess of nitric acid is passed rapidly through a narrow metal tube at 400 – 500°C (vapour phase nitration) one hydrogen atom of the alkane is substituted by nitro ($-NO_2$) group.

$$\mathrm{CH_4} + \mathrm{HONO_2} \longrightarrow \underset{\text{Nitro-methane}}{\mathrm{CH_3-NO_2}} + \mathrm{H_2O}$$

Since the vapour phase nitration is carried out at a higher temperature some of the carbon bonds are also attacked resulting in the formation of mixture of nitro derivatives including those of lower alkanes. Thus ethane and propane give the following products.

$$\underset{\text{Ethane}}{CH_3-CH_3} \xrightarrow{HNO_3} \underset{\text{Nitro-ethane}}{CH_3-CH_2-NO_2} + \underset{\text{Nitro-methane}}{CH_3NO_2} + H_2O$$



$$\underset{\text{Propane}}{CH_3-CH_2-CH_3} \xrightarrow{HNO_3} \underset{\text{1-Nitro-propane}}{CH_3-CH_2-CH_2-NO_2} + \underset{\text{2-Nitro-propane}}{CH_3-\underset{NO_2}{\underset{|}{CH}}-CH_3}$$

$$+ \underset{\text{Nitro-methane}}{CH_3-NO_2} + \underset{\text{Nitro-ethane}}{CH_3-CH_2-NO_2} + H_2O$$

(*ii*) **Combustion (Oxidation)** : Hydrocarbons in the presence of oxygen at high temperature burn to form CO_2 and H_2O . In the process of combustion of hydrocarbons much heat is evolved and thus the combustion reactions are extremely exothermic. The inflammability depends upon the volatility of the hydrocarbon. The heat of combustion of the hydrocarbons is a very useful source of heat and power.

$$\underset{\text{methane}}{CH_4} + 2O_2 \longrightarrow CO_2 + 2H_2O \quad \Delta H = -213 \text{ K. Cal mole}^{-1}$$

(*iii*) **Pyrolysis or Cracking** : Pyrolysis (Greek - pyro-fire : lysis-loosing) is the decomposition of a compound by the action of heat alone. Pyrolysis of alkanes particularly of petroleum is also called cracking.

When the vapours of higher alkanes are heated at elevated temperature (500°C or above) in the absence of oxygen, chemical decomposition occurs in two ways.

(1) By fission of C – H linkages to form an unsaturated hydrocarbon and hydrogen gas.

(2) By fission of C – C linkages to give simpler hydrocarbons, one alkane and one alkene.

Thus methane yields carbon and hydrogen as final products.

Example:

$$CH_4 \longrightarrow \underset{\text{(Carbon black)}}{C} + 2H_2$$

(fission of C–H bond).

$$\underset{\text{Butane}}{CH_3 - CH_2 - CH_2 - CH_3} \xrightarrow{600^\circ C} \underset{\text{ethane}}{CH_3 - CH_3} + \underset{\text{ethene}}{CH_2 = CH_2}$$

$$+ \underset{\text{methane}}{CH_4} + \underset{\text{propene}}{CH_3 - CH{=}CH_2}$$

$$\text{and } \underset{\text{2–Butene}}{CH_3 - CH = CH - CH_3} + H_2$$

(Fission of C – C and C – H bonds).

Higher alkanes on cracking give hydrogen and mixtures of alkanes and alkenes having varying number of carbon atoms. Thus cracking process is of great importance to the petroleum industry, because it provides a means for making smaller and more volatile hydrocarbon molecules from the larger and less volatile molecules. Gasoline (motor fuel) obtained by the distilation of natural petroleum cannot meet the increasing demands of motor fuel. Therefore , large quantities and better qualities of gasoline are commercially obtained by the process of cracking of the hydrocarbons.

UNSATURATED HYDROCARBONS

(A) Alkenes or Olefins

As mentioned earlier an alkene has one double bond between two carbon atoms. The general molecular formula of alkenes is C_nH_{2n}. For example, the alkene with two carbons will have four hydrogens (C_2H_4) and an alkene with three carbons will have six hydrogens with the molecular formula C_3H_6. It is quite obvious from the general formula of alkenes that they have less hydrogens than the corresponding alkanes. It means more hydrogen atoms or other atoms or groups can be added to alkenes. Therefore, alkenes are called unsaturated hydrocarbons. Alkenes also make a homologous series and each member of the series has one methylene group (CH_2–) less than the next higher member.

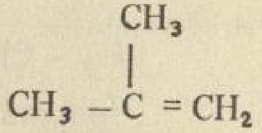
Nomenclature :-

Common System : Common name of an alkene is derived from the name of alkyl group having the same carbon skeleton. The ending-ene is added to the name of corresponding alkyl group.

Examples :

$CH_2 = CH_2$
Ethylene

$CH_3 - CH = CH_2$
Propylene



$CH_3 - \overset{CH_3}{\overset{|}{C}} = CH_2$

Isobutylene

The isomers of butylene and those of higher alkenes are distinguished by putting Greek letters – α, β, γ etc.

$CH_3 - CH_2 - \overset{\beta}{CH} = \overset{\alpha}{CH_2}$
α – Butylene

$\overset{\alpha}{CH_3} - \overset{\beta}{CH} = CH - CH_3$
β – Butylene

Common system of nomenclature is frequently used for simple alkenes but for higher and complicated alkenes IUPAC system is used.

IUPAC System :

Rules for naming alkenes in IUPAC system are as given below :

1. Select the longest continuous carbon chain containing double bond. The ending-ane of the name of corresponding alkane is replaced by ending - ene.

2. Number the carbons of the longest continuous chain containing double bond. The numbering starts from the end which gives smallest possible number to the first doubly bound carbon.

3. For indicating the position of double bond put before the name of alkene the number of the first doubly bound carbon.

4. Positions of the other substituents are indicated by putting before their names the number of carbons bearing the substituents.

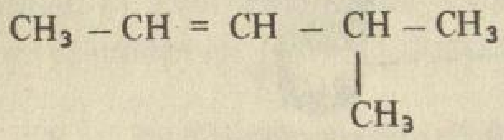
Examples :

$H_2C = CH_2$
Ethene

$CH_3 - CH = CH_2$
Propene

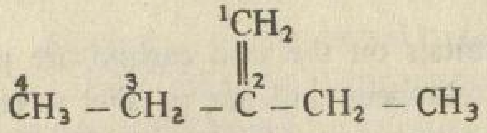
$\overset{4}{C}H_3 - \overset{3}{C}H_2 - \overset{2}{C}H = \overset{1}{C}H_2$
1 – Butene

$\overset{1}{C}H_3 - \overset{2}{C}H = \overset{3}{C}H - \overset{4}{C}H_3$
2 – Butene



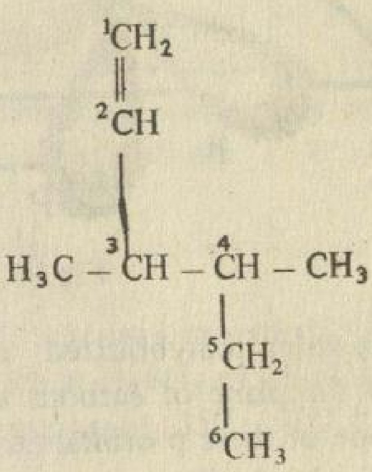
$$CH_3 - CH = CH - \underset{\underset{CH_3}{|}}{CH} - CH_3$$

4 –Methyl– 2 – pentene



$$\overset{4}{C}H_3 - \overset{3}{C}H_2 - \overset{\overset{{}^1CH_2}{\|}}{\overset{2}{C}} - CH_2 - CH_3$$

2 – Ethyl – 1 – butene

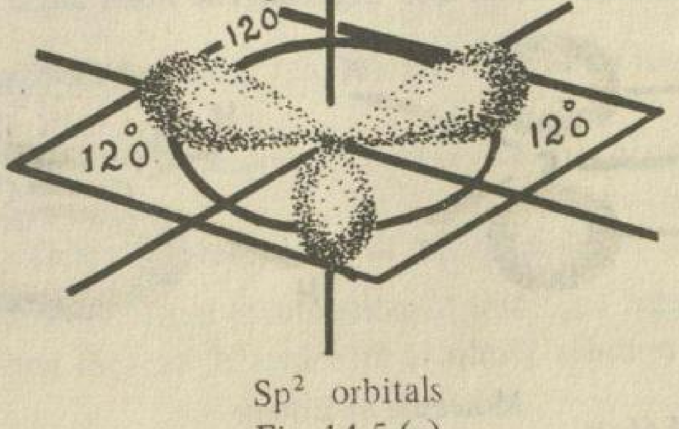


$$H_3C - \overset{\overset{{}^1CH_2}{\overset{\|}{{}^2CH}}}{\overset{|}{{}^3CH}} - \underset{\underset{{}^6CH_3}{\underset{|}{{}^5CH_2}}}{\underset{|}{\overset{4}{C}H}} - CH_3$$

3, 4 – Dimethyl – 1 – hexene

Structure of Ethylene (ethene) :

Ethylene ($CH_2 = CH_2$) is the simplest member of this homologous series. Each of the two carbons is linked with only three atoms. Therefore, on each carbon one 2s and only two 2p orbitals hybridise to give three [sp^2] hybridised orbitals. These three orbitals are arranged in one plane with an angle of 120° between any two hybridised orbitals. The remaining third unhybridised p orbital is perpendicular to the plane of three hybridised orbitals. The two hybridised orbitals of each carbon overlap with s orbitals of two hydrogen atoms and thus make sigma bonds between carbon and hydrogen. The third hybridised orbital of each carbon overlaps with each other forming a sigma bond between two carbons.



Sp^2 orbitals
Fig. 14.5 (*a*)

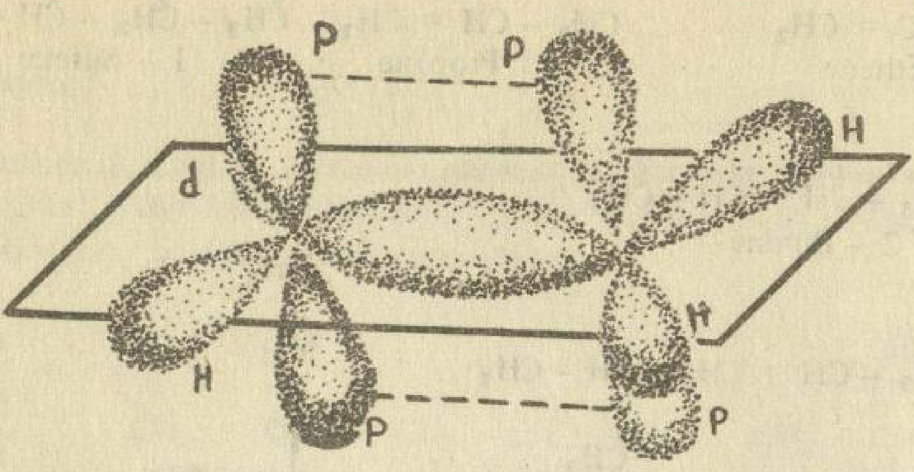
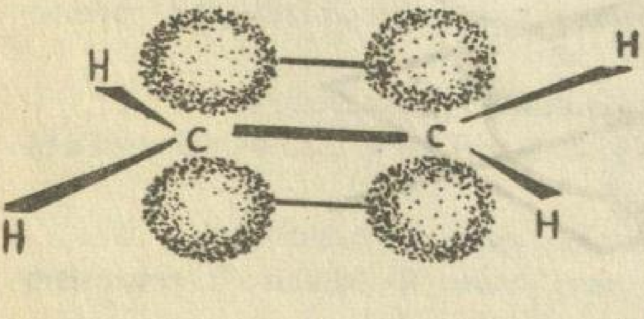
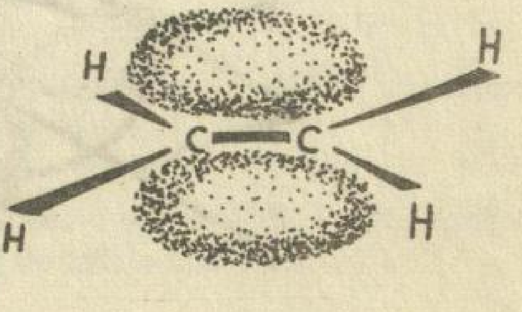


Fig.14.5 (*b*)

The remaining unhybridized p orbitals on the two carbon are perpendicular to the plane of carbons and hydrogens and are parallel to each other. One lobe of these p orbitals is above and second lobe below the plane of hybridised orbitals. These two p orbitals, one on each carbon overlap sidewise with each other forming another covalent bond between two carbons. Since these two p orbitals are parallel to each other the overlapping will not be so effective as in the case of hybridised orbitals of the two carbons. Due to this less overlapping the covalent bond thus formed will be weaker than the carbon - carbon bond due to overlapping of hybridised orbitals. This weaker bond formed by side ways overlapping of two p orbitals is known as π (pi) bond. Unlike the σ bond the electronic density of bond is not cylindrically symmetrical about the line joining the two nuclei of carbons . One sheath of electrons is above the plane of the atoms and the other sheath of electrons is below this plane. Thus these electrons are exposed and can be readily attacked by an electrophile. Thus due to the presence of double bond, alkenes will act as nucleophiles. The characteristic chemical properties of alkenes are due to this peculiar electronic arrangement of electrons. The double bond in alkenes consists of one stronger σ bond and one weaker π bond. Ethylene molecule is flat and trigonal. The bond angle between two





Molecule of Ethene

Fig. 14.6(*a*)

Fig. 14.6(*b*)

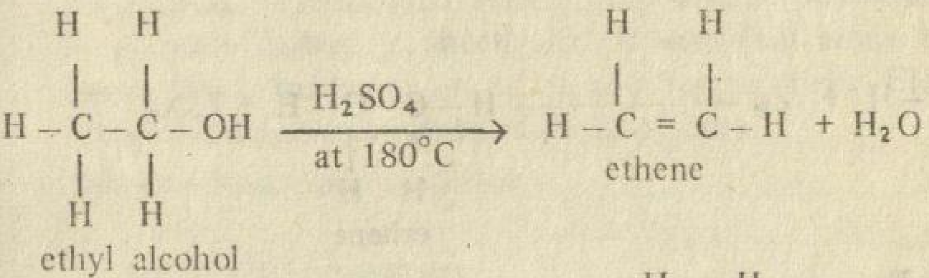
C–H bond is 116. 7°, the bond-angle between C – H and C – C bonds is 121.6. The bond length of carbon-carbon double bond is 1.34 A° and that of C – H bond is 1.10A°.

General Methods of Preparation of Alkenes :

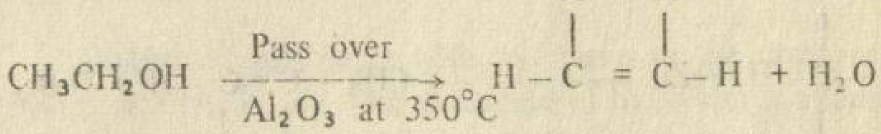
Alkenes of commercial importance are obtained by the cracking of petroleum. Alkenes can also be synthesised in laboratories. The important methods of their preparation involve *elimination reactions* in which two atoms or groups are removed from the adjacent carbons.

1. By the dehydration of alcohols.

Alcohols are dehydrated to produce alkenes (removal of H_2O) by heating (at 180°C) them with strong acids such as H_2SO_4 or H_3PO_4. Alcohols can also be dehydrated by passing their vapours at (350 – 400°C), over acidic catalyst such as alumina (Al_2O_3).



$$\underset{\text{ethyl alcohol}}{H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-OH} \xrightarrow[\text{at } 180^\circ C]{H_2SO_4} \underset{\text{ethene}}{H-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-H} + H_2O$$



$$CH_3CH_2OH \xrightarrow[Al_2O_3 \text{ at } 350^\circ C]{\text{Pass over}} H-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-H + H_2O$$

even P_2O_5 may be employed.

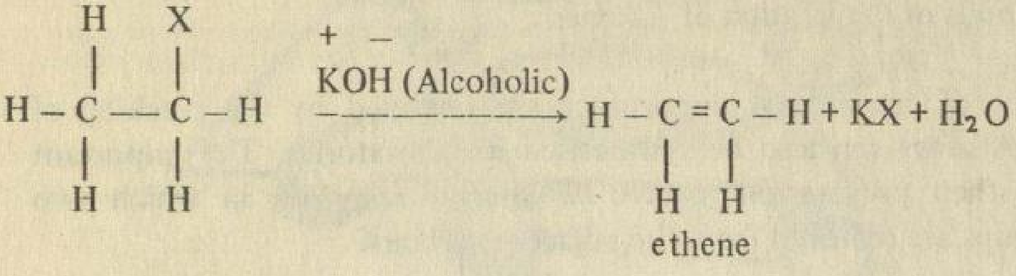
$$CH_3CH_2OH + P_2O_5 \xrightarrow[\text{gently}]{\text{Warm}} H_2C = CH_2 + H_3PO_4$$

The order in ease of dehydration of alcohols is as below :

Tertiary alcohols > secondary alcohols > primary alcohols.

2. By Dehydrohalogenation of Alkyl halides.

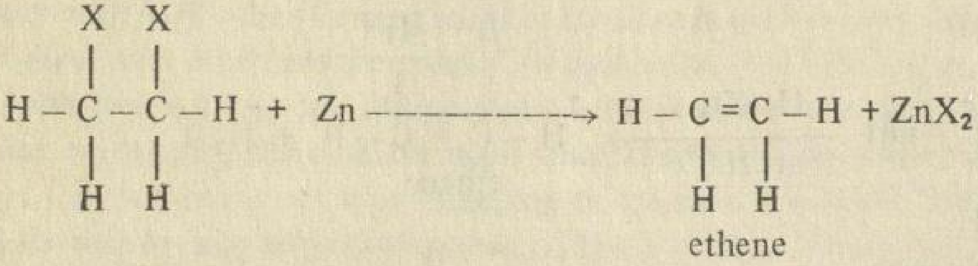
Dehydrohalogenation (elimination of hydrogen halide) of alkyl halides takes place when they are heated with alcoholic solution of potassium hydroxide and in this elimination reaction halogen is removed from one carbon and hydrogen from the adjacent carbon forming a double bond between the two carbons.



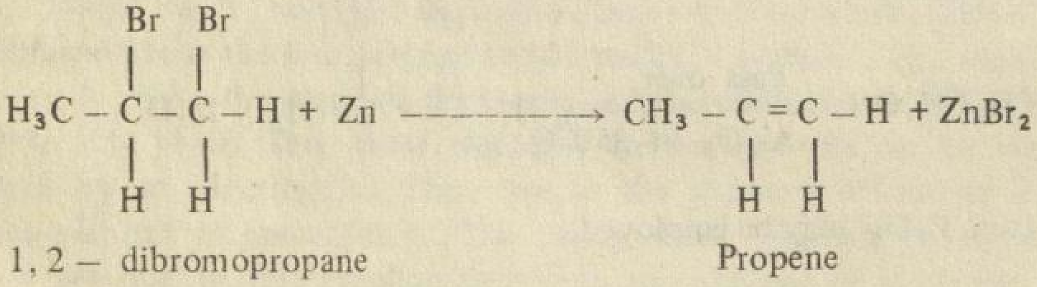
$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{X}{C}}-H \xrightarrow{\overset{+\ \ -}{KOH}\text{ (Alcoholic)}} \underset{\text{ethene}}{H-\underset{H}{C}=\underset{H}{C}-H} + KX + H_2O$$

3. By Dehalogenation of Vicinal Dihaloalkane with Zinc.

Dihaloalkanes having halogens at the adjacent carbons are known as vicinal dihaloalkanes. When vicinal dihaloalkanes are treated with zinc dust they lose halogen atoms producing alkenes.



$$H-\underset{H}{\overset{X}{C}}-\underset{H}{\overset{X}{C}}-H + Zn \longrightarrow \underset{\text{ethene}}{H-\underset{H}{C}=\underset{H}{C}-H} + ZnX_2$$



$$\underset{\text{1, 2 – dibromopropane}}{H_3C-\underset{H}{\overset{Br}{C}}-\underset{H}{\overset{Br}{C}}-H} + Zn \longrightarrow \underset{\text{Propene}}{CH_3-\underset{H}{C}=\underset{H}{C}-H} + ZnBr_2$$

General Properties of Alkenes.

Physical Properties :

1. The first three alkenes, ethene, propene and butenes are gases at ordinary temperature. The next fourteen members are liquids while the higher alkenes are solids.

They are all colourless and odourless, except ethene, which has a rather pleasant odour.

2. They are less volatile than the corresponding alkanes.

3. They are almost insoluble in water, but dissolve freely in organic solvents.

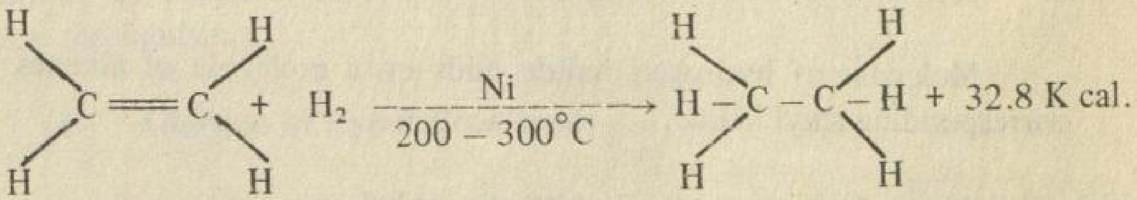
4. Their melting points, boiling points and specific gravities in general, rise with increase of molecular weights in the homologous series.

Chemical Properties: Earlier it has been mentioned that double bond in alkenes consists of one strong sigma bond (bond energy about 60K cal/mole) and a weaker π bond (bond energy above 40K cal/mole). The cloud of π electrons is above and below the plane of atoms and is thus exposed to an electrophile. Therefore π bond will be attacked easily and less energy will be required to break it. When an electrophile attacks on a double bond of an alkene the π bond is broken down and two new sigma bonds one with each carbon, are formed. Thus an unsaturated compound is converted into a saturated in which each carbon is directly linked with four atoms through four sigma bonds. Such reactions are called addition reactions. Electrophilic addition is the characteristic property of all the alkenes.

Addition Reactions of Alkenes :

(1) Hydrogenation :

Alkenes readily react with hydrogen in the presence of a metal as a catalyst like Ni, Pt, Pd. One molecule of hydrogen is added to one molecule of alkene to give one molecule of alkane. Hydrogenation is an exothermic reaction :



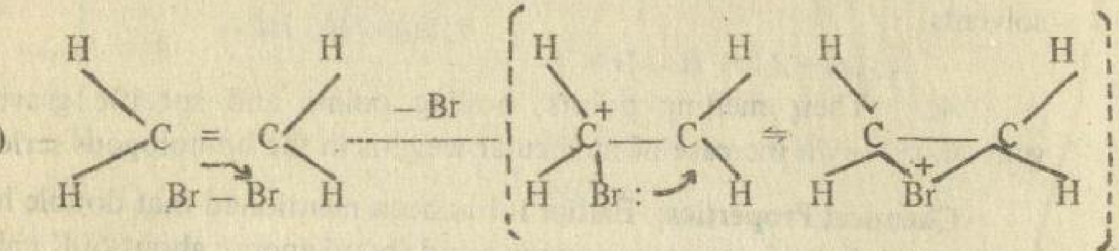
Ethene Ethane

(2) Addition of Halogens :

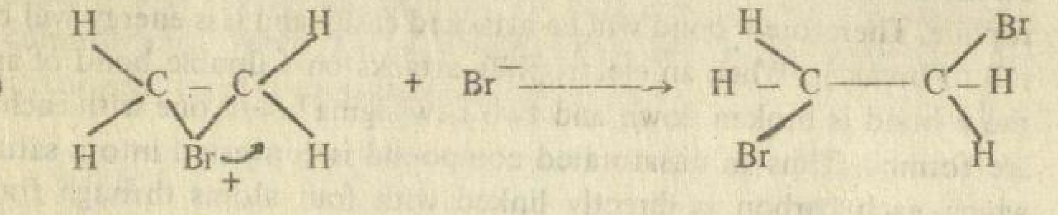
Chlorine and bromine add readily to double bond of alkenes producing vicinial dihaloalkanes. Fluorine cause extensive fragmentations of the molecule. Vicinial di-iodides are unstable and are readily reconverted into alkenes.

Halogenation of alkenes is believed to proceed theough the following mechanism ;

(*i*)



(*ii*)



1, 2 – Dibromoethane

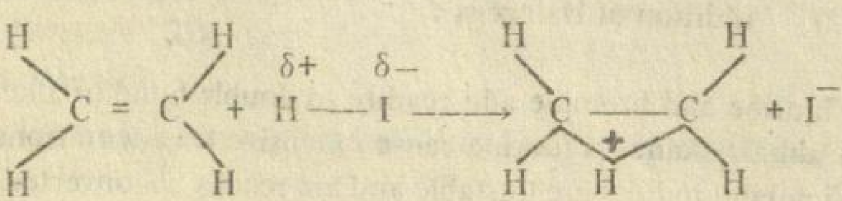
The same mechanism is followed by all electrophilic addition reactions of alkenes. When bromine water is added to an organic compound containing carbon-carbon double bond, the red colour of bromine water disappears due to addition of bromine at the double bond. This is a very convenient test for detecting the presence of carbon-carbon double bond in an organic compound.

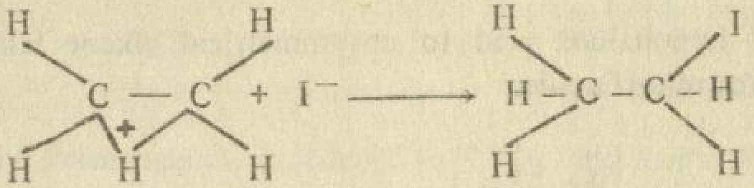
(3) Addition of Hydrogen Halides (Halogen Acids) :

Molecule of hydrogen halide adds on a molecule of alkenes to give corresponding alkyl halide.

The order in the ease of addition is as below :-

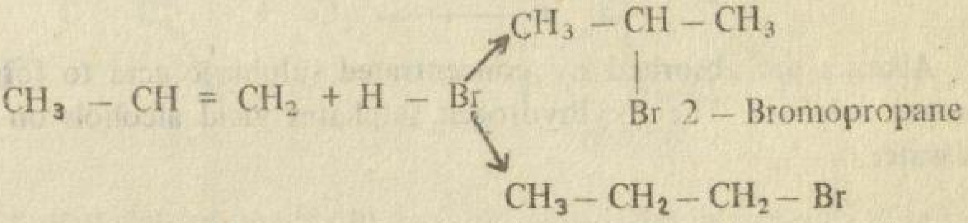
$$HI > HBr > HCl > HF$$





Ethyl iodide or Iodoethane

Ethene is a symmetrical molecule and only one product is possible whether hydrogen or hydrogen halide is attached with any one of the two carbons. In case of unsymmetrical molecules like propylene, the addition of hydrogen halides may produce two isomeric products.



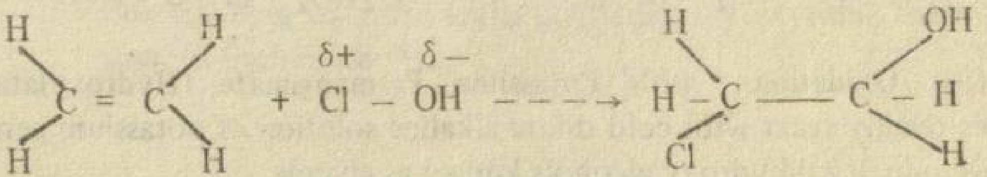
2 – Bromopropane

1 – Bromo propane

The same situation may arise in the addition of any unsymmetrical molecule to an unsymmetrical alkene. In most of these cases, however only one product is obtained. For example in the above reaction of propene only 2– Bromopropane is obtained. For such reactions Markownikoff gave a rule which is known as Markow-nikoff's rule. According to this rule an electrophilic addition of unsymmetrical molecule to unsymmetrical alkene, the positive part of the adding molecule is attached to the carbon having larger number of hydrogen atoms attached. This rule applies to all electrophilic additions of alkenes but not to those additions proceeding through free radical mechanism.

(4) Addition of Hypohalous Acids :

Aqueous solutions of hypohalous acids react with alkenes to give halohydrins. Organic compounds having hydroxyl group and halogen at the adjacent carbons are referred as halohydrins.

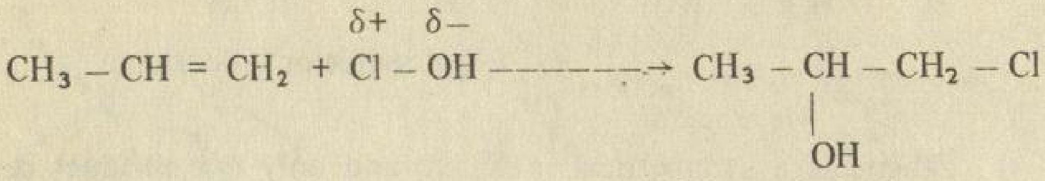


Ethylene chlorohydrin

or

1 – chloro – 2 – hydroxyethane.

Addition of hypohalous acid to unsymmetrical alkene takes place according to Markownikoff's rule.



$$CH_3-CH=CH_2+\overset{\delta+}{Cl}-\overset{\delta-}{OH}\longrightarrow CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-Cl$$

1-Chloro-2-hydroxypropane

(5) **Addition of Sulphuric Acid :**

Alkenes are absorbed by concentrated sulphuric acid to form alkylhydrogen sulphate. The alkylhydrogen sulphates yield alcohols on dilution with water.

$$CH_2=CH_2+H:\ OSO_3H\longrightarrow CH_3-CH_2OSO_3H$$

ethylhydrogen sulphate

$$CH_3-CH_2-OSO_3H+HOH\longrightarrow CH_3-CH_2OH+H_2SO_4$$

ethyl alcohol

Addition of sulphuric acid to an unsymmetrical olefine takes place according to Markownikoff's rule.

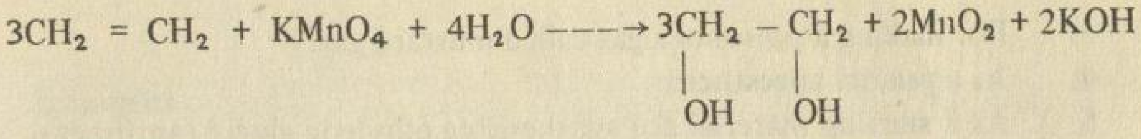
(6) **Oxidation Reactions :**

The carbon double bond is far more susceptible to oxidising agents than the single bond. This property readily distinguishes alkenes from the alkanes.

(*i*) Combustion :- Alkenes burn in air producing CO_2 and H_2O alongwith a large amount of heat.

$$CH_2=CH_2+3O_2\longrightarrow 2CO_2+2H_2O+\text{Heat}$$

(*ii*) **Oxidation with Potassium Permanganate (Hydroxylation):-** Alkenes readily react with cold dilute alkaline solution of potassium permanganate producing dihydroxy alcohols known as glycols.

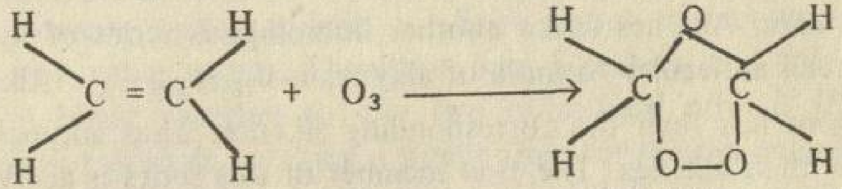


$$3CH_2 = CH_2 + KMnO_4 + 4H_2O \dashrightarrow 3\underset{OH}{\underset{|}{CH_2}} - \underset{OH}{\underset{|}{CH_2}} + 2MnO_2 + 2KOH$$

ethylene glycol

The Permanganate is reduced to MnO_2 and its purple colour disappears. This is a very useful test for the detection of carbon-carbon double bond and is known as Baeyer's test.

(*iii*) **Oxidation with Ozone :-** When ozone is passed through the solution of an alkene it adds on to form an ozonide.



Ozonide

The ozonides are readily hydrolysed with water in presence of reducing agents to produce aldehydes and ketones. Thus the ozonide is broken down into two molecules. This reaction is used to locate the position of a double bond in the compound.

(7) **Polymerisation (Formation of Polyethylene) :**

When liquid ethene is heated to a high temperature under high pressure and in presence of a catalyst it undergoes self-addition reaction (Polymerization) and forms polyethylene (mol. wt. about 20 000). The commercial name of polyethylene is polythene and is used as a plastic material in industries.

$$n\,C_2H_4 \xrightarrow[15000\ \text{PSi}]{100^\circ C} (C_2H_4)_n$$

Polyethylene

Uses of Ethylene : Ethylene is used for producing oxyethylene flame for cutting and welding of metals.

2. For ripening of green fruits artificially by exposing them to the gaseous hydrocarbons.

3. For making a poisonous gas called mustard gas.
4. As a general anaesthetic.
5. As a starting material for synthesising ethylene glycol (antifreez), ethylene dichloride (solvent), ethylene oxide (fumigant) and ethyl alcohol etc.
6. For the manufacture of plastics for making bags, table cloths, cables, etc.

(B) ALKYNES OR ACETYLENES

Hydrocarbons having a triple bond between two carbons are known as alkynes or acetylenes. Alkynes make another homologous series of hydrocarbons. The general molecular formula of alkynes is $C_n H_{2n-2}$. Alkynes have two hydrogens less than the corresponding alkenes. Thus alkynes are more unsaturated than alkenes. The first member of this series is acetylene ($HC \equiv CH$). Acetylene is the alkyne which has commercial importance. Acetylene gave its name to the common name for this series, *i.e.* acetylenes. Alkynes rarely occur in nature.

Nomenclature :

Common System : In common system each alkyne is considered to be the alkyl substituted derivative of acetylene. Therefore, in this system alkynes are named by adding the names of alkyl groups before acetylene.

Examples ·

$HC \equiv CH$	$H_3C - C \equiv C - H$	$H_3C - C \equiv C - CH_3$
Acetylene	Methyl acetylene	Dimethyl acetylene

IUPAC System : The longest continuous carbon chain containing triple bond is selected. The ending-ane of the name of the corresponding alkane is replaced by ending-yne.

The rules for numbering the carbons and indicating the positions of triple bonds and other substituents are the same as described in the nomenclature of alkenes.

Examples :

$H - C \equiv C - H$

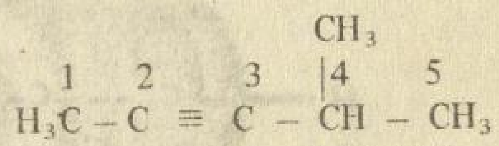
Ethyne

$\overset{3}{H_3C} - \overset{2}{C} \equiv \overset{1}{C} - H$

1 – Propyne

$\overset{1}{H_3C} - \overset{2}{C} \equiv \overset{3}{C} - \overset{4}{CH_3}$

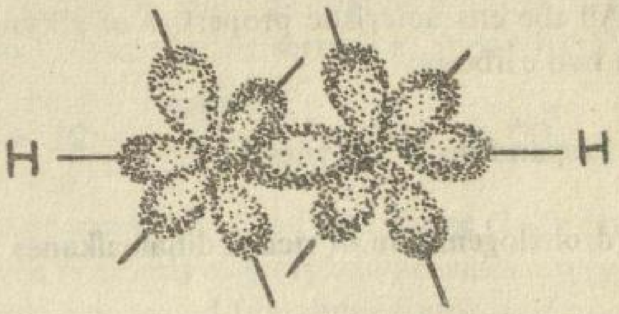
2 – Butyne



$\overset{1}{H_3C} - \overset{2}{C} \equiv \overset{3}{C} - \overset{\overset{CH_3}{|\,4}}{CH} - \overset{5}{CH_3}$

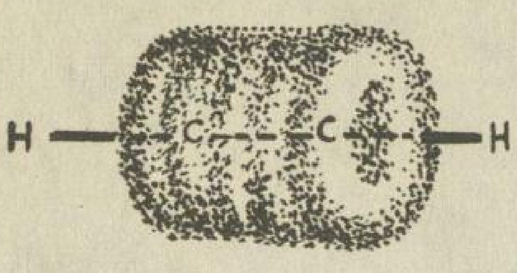
4 – methyl – 2 Pentyne

Structure of acetylene : Each carbon of acetylene is attached with only two other atoms. Therefore, one S orbital and only one P orbital of carbon blend together to give two hybridised orbitals [SP]. These two hybridised orbitals lie along a straight line forming an angle of 180° between the two hybrid orbitals. The two un-hybridised p-orbitals on each carbon atom lie perpendicular to each other and also to [SP] hybrid orbitals.



(Fig.14.7)

One of the [SP] hybrid orbitals, of each carbon, overlaps with S orbital of hydrogen forming a sigma bond (C – H). The other [SP] orbitals of both the carbons overlap with each other along their axes forming a carbon – carbon sigma bond. Now the remaining two P orbitals of one carbon are parallel to the two P orbitals of the second carbon. The two orbitals of one carbon overlap sidewise with the two P orbitals of the second carbon forming two π bonds between the two carbons . The triple bond between two carbons consists of one stronger sigma bond and two weaker π bonds. These four π electrons make a sheath of electronic cloud which is cylindrically symmetrical around the sigma bond.



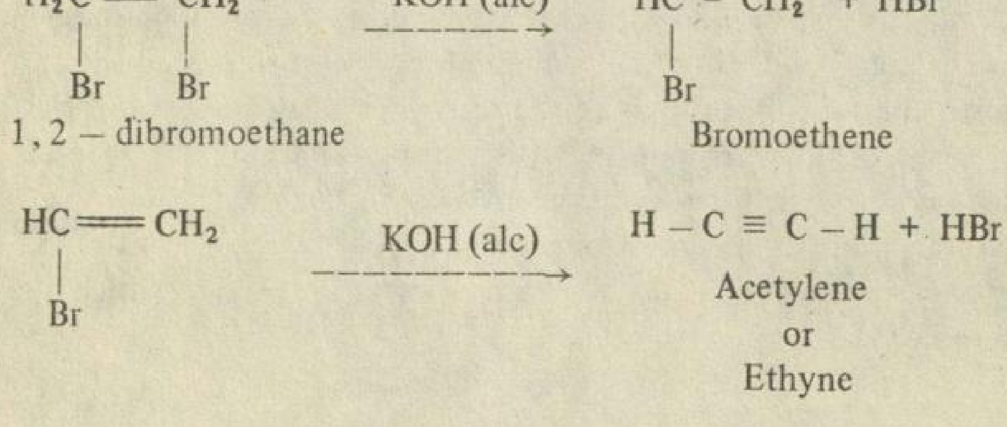
(Fig. 14.8)

All the four atoms of acetylene lie in one straight line and thus the molecule of acetylene is a linear one with an angle of 180° between C – C bonds. Bond length of carbon – carbon triple bond is 1.20A°, which is shorter than carbon-carbon double bond (1.34A°). The bond length of carbon-hydrogen bond is 1.06A°. Bond energy of carbon-carbon triple bond is 120 Kcal./mole. All the characteristic properties of alkynes are due to this triple bond between two carbons.

General Methods of Preparation of Alkynes :

1. **By dehydrohalogenation of vicinal dihaloalkanes :**

Vicinal dihaloalkanes when treated with alcoholic potassium hydroxide lose two molecules of hydrogen halides forming a triple bond between two carbons. The reaction is completed in two steps.

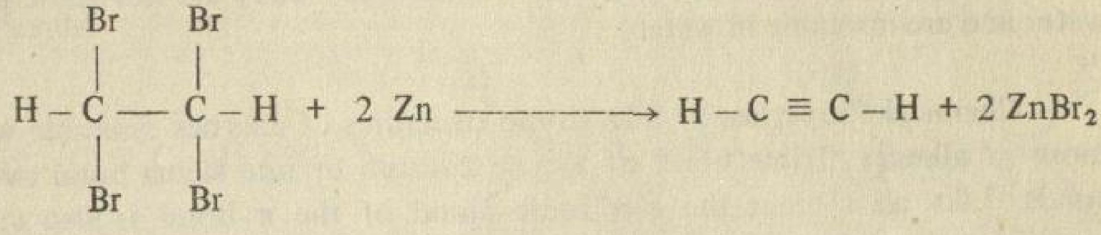


$$\underset{\text{1, 2 – dibromoethane}}{\underset{\mathrm{Br}}{\mathrm{H_2C}} - \underset{\mathrm{Br}}{\mathrm{CH_2}}} \xrightarrow{\text{KOH (alc)}} \underset{\text{Bromoethene}}{\underset{\mathrm{Br}}{\mathrm{HC}} = \mathrm{CH_2}} + \mathrm{HBr}$$

$$\underset{\mathrm{Br}}{\mathrm{HC}} = \mathrm{CH_2} \xrightarrow{\text{KOH (alc)}} \underset{\substack{\text{Acetylene} \\ \text{or} \\ \text{Ethyne}}}{\mathrm{H - C \equiv C - H}} + \mathrm{HBr}$$

2. **By dehalogenation of tetrahaloalkanes** :

Tetrahaloalkanes on treatment with Zn dust produce alkynes.



$$H-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{C}}-H + 2\,Zn \longrightarrow H-C \equiv C-H + 2\,ZnBr_2$$

Commercial Preparation of Acetylene.

The two important commercial methods for the preparation of acetylene are described below :

(*i*) **From calcium carbide (CaC_2)** :: Acetylene is commercially obtained by the hydrolysis of calcium carbide (CaC_2) by water.

$$CaC_2 + 2H_2O \longrightarrow \underset{\text{Acetylene}}{H-C \equiv C-H} + Ca(OH)_2$$

Calcium Carbide is obtained by heating calcium oxide (from limestone) and coke (from coal) in an electric furnace at about 3000°C.

$$CaO + 3C \xrightarrow{3000^\circ C} CaC_2 + CO$$

Thus acetylene can be obtained from three cheap raw materials – lime, coal and water. This synthesis of acetylene provides a very good example of preparing an organic compound from purely inorganic materials.

(*ii*) **From methane** : Acetylene can also be obtained on commercial scale by heating natural gas, especially methane, at a high temperature.

$$2CH_4 \xrightarrow{1400\ -\ 1600^\circ C} HC \equiv CH + H_2$$

General Properties of Alkynes :

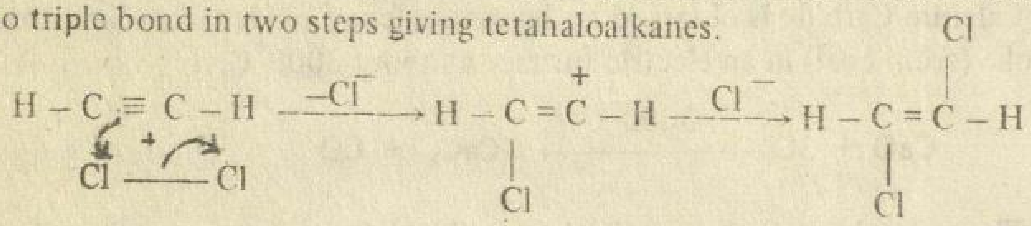
Physical Properties :

In their physical properties alkynes resemble with alkenes and alkanes. The first three members (acetylene, propyne, 1-butyne) are gases at room temperature. The other alkynes are liquids and solids. Their boiling points , melting points and densities are generally somewhat higher than the corresponding alkanes or alkenes. Alkynes also show a regular change in their physical properties with increase in the chain length. They are less dense than water and are insoluble in water.

Chemical Properties : Electronic structures of alkynes resemble with those of alkenes. Triple bond of alkyne consists of one sigma bond two π bonds. Like all alkenes the electronic cloud of the π bond is also quite exposed and can be attacked by electrophilic reagents. Like alkenes, alkynes also undergo electrophilic addition reactions with the difference that in case of alkynes two molecules of the reagent are added to triple bond. Due to the presence of two π bonds in alkynes it can be expected that triple bond should be more reactive towards electrophilic reagents than the double bond in alkenes. But actually the triple bond of alkynes are less reactive towards electrophiles and thus alkynes are less nucleophilic than alkenes.

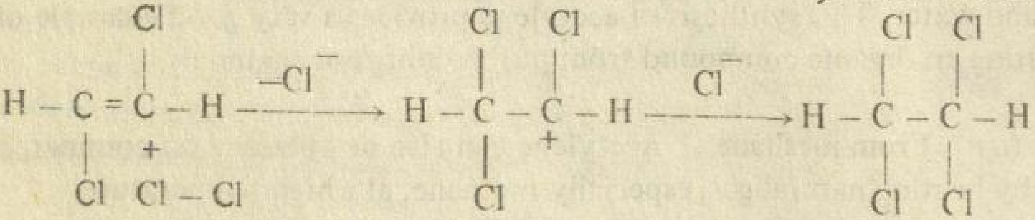
1. Addition Reactions of Alkynes :

(*i*) **Addition of Halogens :** Two molecules of chlorine and bromine add to triple bond in two steps giving tetahaloalkanes.



$$H-C\equiv C-H + Cl-Cl \xrightarrow{-Cl^-} H-\underset{Cl}{C}=\overset{+}{C}-H \xrightarrow{Cl^-} H-\underset{Cl}{C}=\overset{Cl}{C}-H$$

1,2–dichloroethene.



$$H-\underset{Cl}{C}=\overset{Cl}{C}-H + Cl-Cl \xrightarrow{-Cl^-} H-\underset{Cl}{\overset{Cl}{C}}-\overset{Cl}{\overset{+}{C}}-H \xrightarrow{Cl^-} H-\underset{Cl}{\overset{Cl}{C}}-\underset{Cl}{\overset{Cl}{C}}-H$$

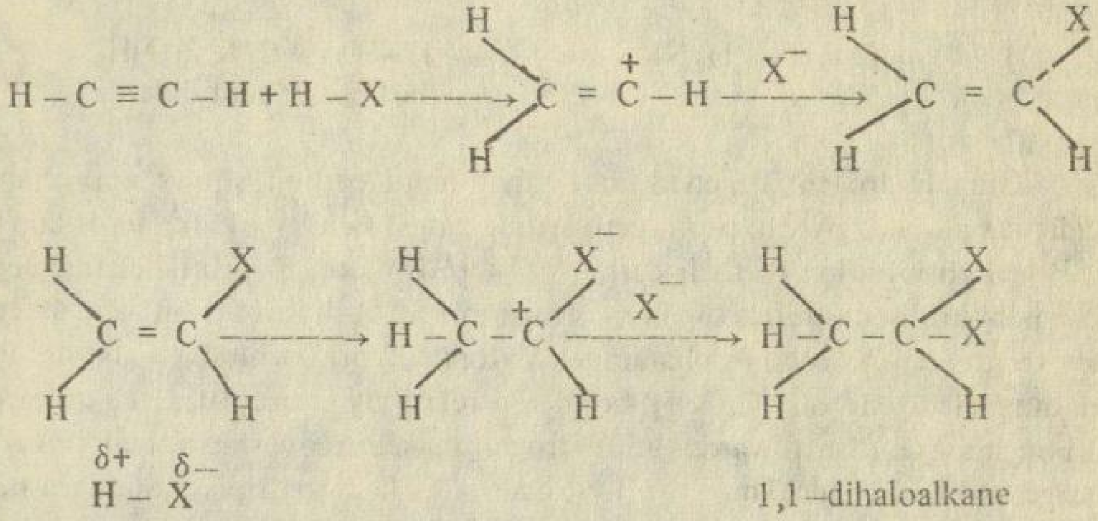
1,1,2,2–tetrachloroethane.

It is possible to stop the reaction at dihaloalkene stage by using proper conditions of reaction.

$FeCl_3$ is often used as a catalyst in this addition reaction because $FeCl_3$ polarises the halogen-halogen bond (*e.g.*, $\overset{\delta+}{Cl}-\overset{\delta-}{Cl}$........ $FeCl_3$).

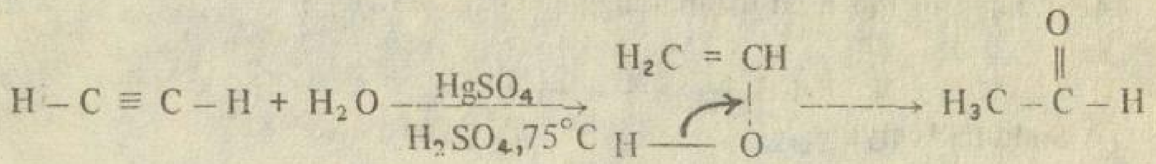
Thus halogen molecule becomes a better electrophile in presence of $FeCl_3$. Iodine reacts with alkynes very slowly to give 1 , 2 - di-iodoethene.

(*ii*) **Addition of Hydrogen Halide** : Hydrogen halides (HCl, HBr, HI) add to the triple bond in two steps producing 1,1-dihaloalkanes. Addition of hydrogen halides to unsymmetrical alkynes takes place according to Markownikoff's rule.



1,1–dihaloalkane

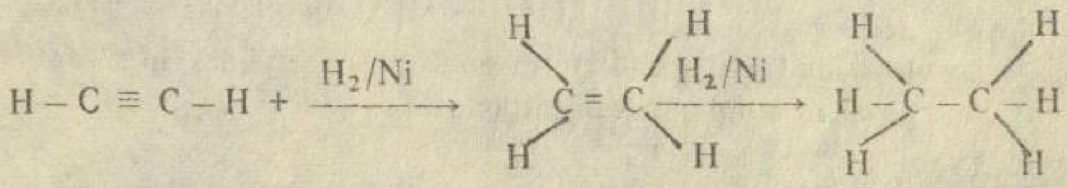
(*iii*) **Addition of Water** : Water adds to acetylene in the presence of mercuric sulphate in aqueous sulphuric acid to give acetaldehyde as the final product.



ethenol
or
vinyl alcohol

Acetaldehyde

(*iv*) **Addition of Hydrogen** : Hydrogen adds to alkynes in presence of finely divided Ni or Pd or Pt to give alkanes



ethene ethane

Alkynes may be partially reduced to alkenes by sodium in liquid ammonia

$$HC \equiv CH + H_2 \xrightarrow[\text{Na and liq.ammonia}]{} \underset{\text{Ethene}}{H_2C = CH_2}$$

2. Acidity of 1-alkynes :

1-Alkynes react with strong bases like sodium or potassium in liquid ammonia ($NaNH_2$) to give the salts known as acetylides.

$$H-C\equiv C-H + H_2\overset{-}{N}\overset{+}{K} \longrightarrow H-C\equiv \overset{-}{C}\,\overset{+}{K} + NH_3$$

Potassium acetylide

Thus hydrogen attached to triply bound carbon shows appreciable acidity as alkynes give up protons to strong bases. Acidity of alkynes is due to [SP] hybridisation of their carbons. There is more S orbital character in [SP] hybridised orbitals of alkynes than in [SP^2] hybrid orbitals in alkene. Due to greater S orbitals character of atomic hybrid orbitals of alkynes the bonding electrons of C – H bond are relatively more attracted towards carbon nucleus than towards the hydrogen nucleus rendering a small positive charge on hydrogen. Thus the hydrogen attached to triply bound carbon can be removed in the form of proton with the help of a strong base. Acetylene is less acidic than water and 10^{13} times more acidic than ammonia and about 10^{18} times more acidic than ethene or ethane.

Acetylides may be used for making higher alkynes, *e.g.*,

$$\underset{\text{Sodium Acetylide}}{H-C\equiv \overset{-}{C}\;\overset{+}{Na}} + CH_3I \longrightarrow \underset{\text{Propyne}}{H-C\equiv C-CH_3} + \overset{+}{Na}\overset{-}{I}.$$

Acetylenes also react with ammonical silver nitrate $\overset{+}{[Ag(NH_3)_2]}\;\overset{-}{NO_3}$ to give a very useful test for detecting the presence of carbon-carbon triple bond in an organic compound.

$$H-C\equiv C-H + [Ag(NH_3)_2]^{+} \longrightarrow H-C\equiv C-Ag + NH_3 + \overset{+}{NH_4}$$

It is to be noted that unlike sodium or potassium acetylides, in silver acetylide there is a covalent bond between carbon and silver.

3. Combustion : Alkynes burn in air forming water and carbon dioxide. By combustion of acetylene with pure oxygen a flame of about 2800°C can be obtained. Acetylene gives higher flame temperature than ehtane or ethene.

$$2HC \equiv CH + 5O_2 \xrightarrow{\qquad} 4CO_2 + 2H_2O + \text{Heat}$$

Acetylene burns with a white and bright flame.

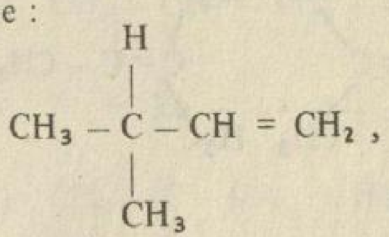
Commercial Uses of Acetylene :

(*i*) Oxyacetylene flame is used for cutting and welding of metals. About one fourth of annual production of acetylene is used in oxyacetylene flame. For welding purposes acetylene is dissolved under 200 PSi pressure in acetone and packed in cylinders containing suitable porous material.

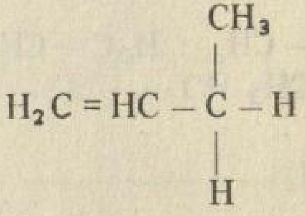
(*ii*) Acetylene is also used commercially as a starting material for synthesis of many important organic compounds like vinyl acetate (used in plastic)alcohols, acrylonitrile which is polymerised to form synthetic fibre and synthetic rubber.

QUESTIONS

1. Classify the following hydrocarbons into alkane, alkene and alkyne :

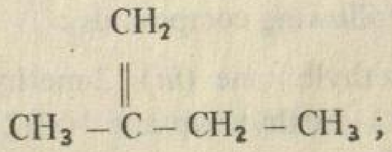


$CH_3-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH=CH_2$,



$H_2C=HC-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-H$; 1 – Hexyne ; $CH_3-CH_2-CH_3$;

C_4H_8 ;



$CH_3-\overset{\overset{CH_2}{\|}}{C}-CH_2-CH_3$; C_5H_8 ; 2 – Pentene and 2 – methyl butane.

2. (*a*) Write molecular formula of next higher homologue of each of the following :

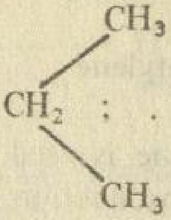
C_2H_6 ; C_4H_6 ; C_5H_{10} ; C_4H_8 ; C_7H_{16} ; C_5H_8 and C_3H_6

(*b*) Arrange the following into homologous series :

C_3H_8 ; C_5H_8 ; C_6H_{12} ; C_5H_{10} ; C_8H_{18} ; C_6H_{10} ; and C_4H_8

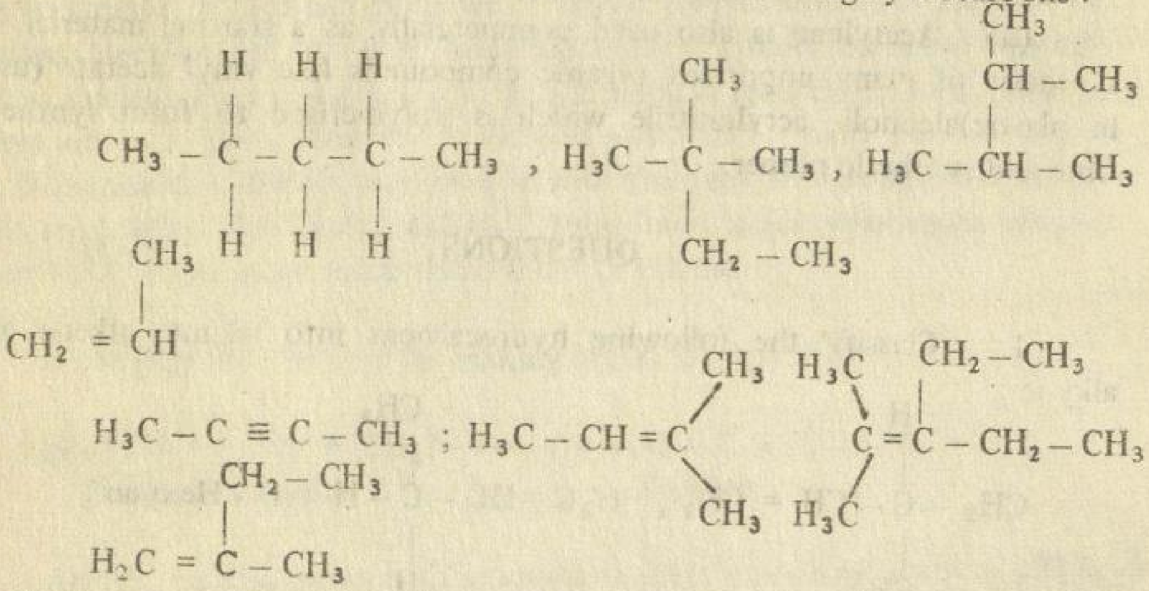
Which of the above compounds will resemble in their properties with those of C_8H_{16}.

3. Which of the following hydrocarbons will give addition reactions and which will give substitution reactions :

$CH_3-C\equiv C-CH_3$;  : . C_5H_{10} ; C_2H_2 : propene

Pentyne ; 3 - ethylhexane and heptane.

4. (*a*) Give I.U.P.A.C. names to the following hydrocarbons :



$CH_3-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-CH_3$, $H_3C-\overset{CH_3}{\underset{CH_2-CH_3}{C}}-CH_3$, $H_3C-\overset{\overset{\overset{CH_3}{|}}{CH-CH_3}}{\overset{|}{CH}}-CH_3$

$CH_2=\overset{\overset{CH_3}{|}}{CH}$

$H_3C-C\equiv C-CH_3$;

$H_2C=\overset{\overset{CH_2-CH_3}{|}}{C}-CH_3$

(*b*) **Make structure of the following compounds :**

(*i*) Neo-Octane (*ii*)2,2-dimethylbutane (*iii*) 2-methyl – 2 – pentene (*iv*) 1–pentyne (*v*) 3–ethyl–2–methyl heptane (*vi*)2,2–dimethyl 3–hexyne (*vii*) Neoheptane (*viii*) Iso-octane.

5. Why do the four hybridised orbitals of carbon orient towards the four corners of a regular tetrahedron ? What will be the angle between two hybridised orbitals if the hybridised orbitals of carbon orient towards four corners of a square?

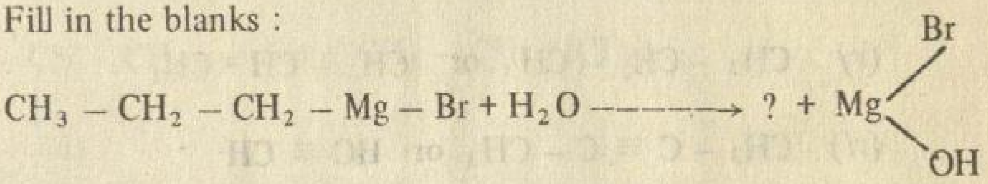
6. (*a*) Which of the following will be the most stable arrangement for the three hybridised orbitals : (*i*) With an angle of 90° between any two orbitals. (*ii*) With an angle of 45° between any two of the orbitals. (*iii*) With an angle of 120° between any two orbitals. Give reasons for your answers.

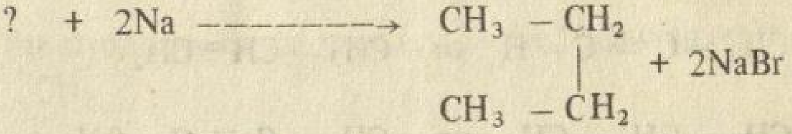
(*b*) Arrange the following in the increasing order of their bond lengths :

$$C = C \; ; \; C \equiv C \text{ and } C - C.$$

7. Is it possible to make a pi bond between carbon and hydrogen ? Is it possible to link two carbons together only through a pi bond without a sigma bond between them ? Explain your answers.

8. Fill in the blanks :

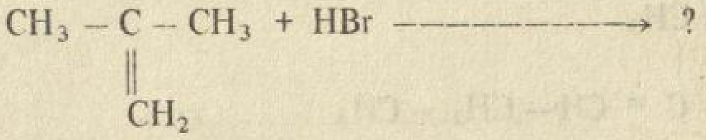
(*i*) 
$CH_3 - CH_2 - CH_2 - Mg - Br + H_2O \longrightarrow ? + Mg\begin{matrix}\diagup Br\\ \diagdown OH\end{matrix}$

(*ii*) 
$? + 2Na \longrightarrow \begin{array}{l}CH_3 - CH_2\\ \qquad\quad |\\ CH_3 - CH_2\end{array} + 2NaBr$

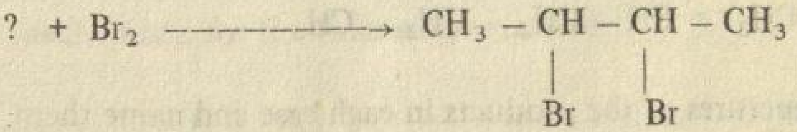
(*iii*) $CH_3 - CH_2 - CH_3 + 5\,O_2 \longrightarrow ? + 4H_2O$

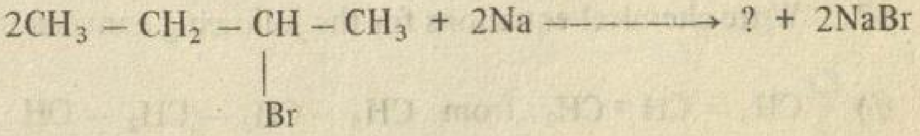
(*iv*) $CH_3 - CH_2 - CH_2 - CH_2 - OH \xrightarrow{H^+} ? + H_3\overset{+}{O}$

(*v*) $? + Zn \longrightarrow CH_3 - CH = CH_2 + ZnBr_2$

(*vi*) 
$CH_3 - \underset{\underset{CH_2}{\|}}{C} - CH_3 + HBr \longrightarrow ?$

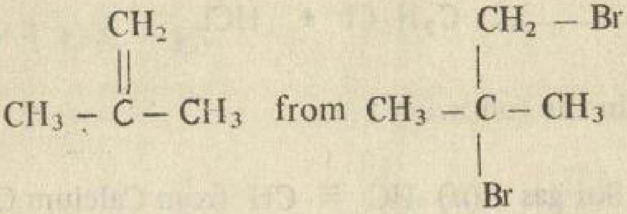
(*vii*) $CH_3 - C \equiv C - H + HOCl \longrightarrow ?$

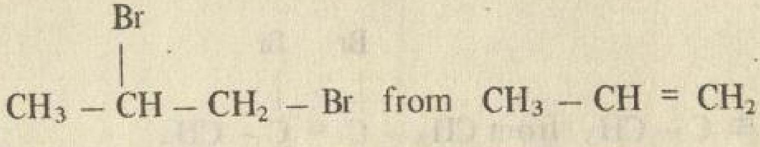
(*viii*) 
$? + Br_2 \longrightarrow CH_3 - \underset{\underset{Br}{|}}{CH} - \underset{\underset{Br}{|}}{CH} - CH_3$

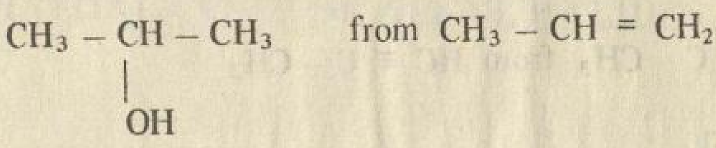
(ix) 
$2CH_3 - CH_2 - \underset{\underset{Br}{|}}{CH} - CH_3 + 2Na \longrightarrow ? + 2NaBr$

9. Which one in each of the following pairs has higher m.p. or b.p

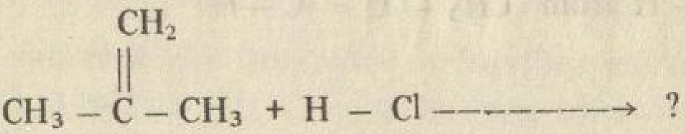
(*i*) $CH_3 - CH_2 - CH_3$ or $CH_3 - CH_2 - CH_2 - CH_3$

(*iii*) 
$CH_3-\overset{\overset{\displaystyle CH_2}{\|}}{C}-CH_3$ from $CH_3-\underset{\underset{\displaystyle Br}{|}}{\overset{\overset{\displaystyle CH_2-Br}{|}}{C}}-CH_3$

(*iv*) 
$CH_3-\overset{\overset{\displaystyle Br}{|}}{CH}-CH_2-Br$ from $CH_3-CH=CH_2$

(*v*) 
$CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_3$ from $CH_3-CH=CH_2$

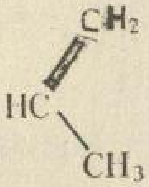
13. Write the structures of the products in the following reactions :

(*i*) 
$CH_3-\overset{\overset{\displaystyle CH_2}{\|}}{C}-CH_3+H-Cl\longrightarrow ?$

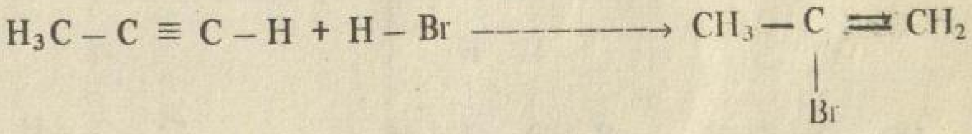
(*ii*) $CH_2=CH-CH_3+HO-Cl\longrightarrow ?$

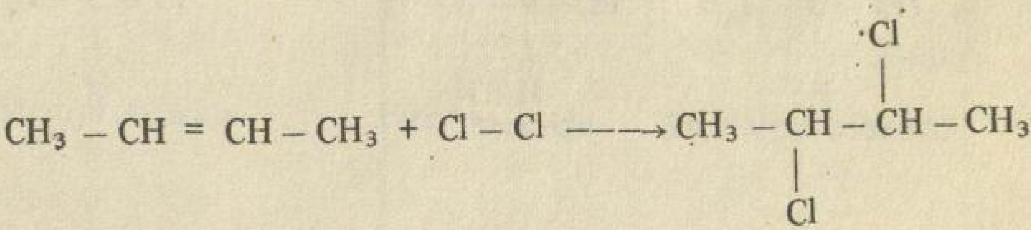
(*iii*) $CH_3-CH=CH_2+2KMnO_4\longrightarrow ?$

(*iv*) $CH_2=CH-CH_2-CH_3+H_2SO_4\longrightarrow ?$

(*v*)  $+ O_3\longrightarrow ?$

14. What do you understand by mechanism of a chemical reaction? Write mechanisms for the following reactions :

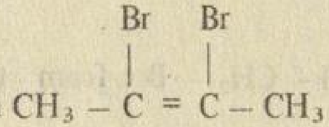
(*i*) 
$H_3C-C\equiv C-H+H-Br\longrightarrow CH_3-\underset{\underset{\displaystyle Br}{|}}{C}=CH_2$

(*ii*) 
$CH_3-CH=CH-CH_3+Cl-Cl\longrightarrow CH_3-\underset{\underset{\displaystyle Cl}{|}}{CH}-\overset{\overset{\displaystyle Cl}{|}}{CH}-CH_3$

(*iii*) $C_2H_6 + Cl_2 \longrightarrow C_2H_5Cl + HCl$

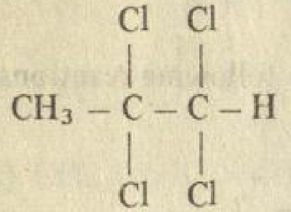
15. How will you obtain the following :

(*i*) $HC \equiv CH$ from Sui gas (*ii*) $HC \equiv CH$ from Calcium Oxide and Coke.



(*iii*) $CH_3 - C \equiv C - CH_3$ from $CH_3 - \overset{\overset{\displaystyle Br}{|}}{C} = \overset{\overset{\displaystyle Br}{|}}{C} - CH_3$

(*iv*) $CH_3 - C \equiv C - CH_3$ from $HC \equiv C - CH_3$



(*v*) $CH_3 - \underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle Cl}{|}}{C}} - \underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle Cl}{|}}{C}} - H$ from $CH_3 - C \equiv C - H$

(*vi*) $CH_3 - CH_3$ from $CH_3CO\overset{-}{O}\overset{+}{Na}$

CHAPTER 15

MONOHALOALKANES OR ALKYL HALIDES AND AMINES

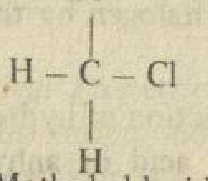
The monohalogen derivatives of Paraffins are known as monohaloalkanes or alkyl halides. The alkyl halides form a homologous series of organic compounds which may be represented with a general formula $C_nH_{2n+1}\cdot X$ or $R-X$ where X is a halogen atom. These are obtained by replacing a hydrogen atom in alkanes with a halogen atom such as Cl, Br or I. Monohaloalkanes may be classified into primary, secondary and tertiary alkyl halides, depending on whether the halogen bearing carbon is primary, secondary or tertiary.

NOMENCLATURE

Common System :

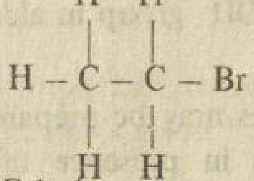
In the Common System the name of the halogen is added after the name of alkyl group to which it is attached. To distinguish various isomers of a monohaloalkane, the prefixes sec- and ter- are used.

Examples:



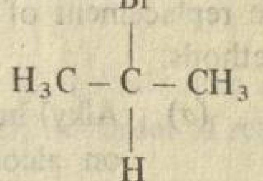
$\mathrm{H-\underset{H}{\overset{H}{C}}-Cl}$

Methyl chloride



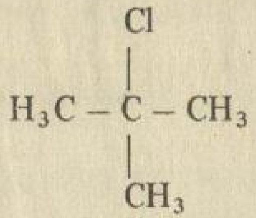
$\mathrm{H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-Br}$

Ethyl bromide



$\mathrm{H_3C-\underset{H}{\overset{Br}{C}}-CH_3}$

Sec-Propyl bromide



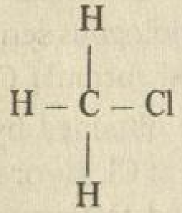
$$H_3C - \overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{C}} - CH_3$$

ter-Butyl chloride

IUPAC System

In the IUPAC System, a monohaloalkane is considered to be the derivative of an alkane containing the same number of carbons as are present in the longest continuous carbon chain of the haloalkane. The method for numbers is the same as described earlier. The position , number and the name of halogen is added before the name of corresponding alkane.

Example :

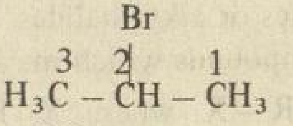


$$H - \overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}} - Cl$$

Chloromethane

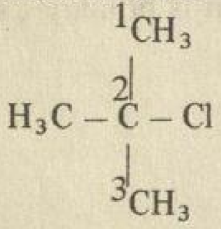
$H_3C - CH_2 - Br$

Bromoethane



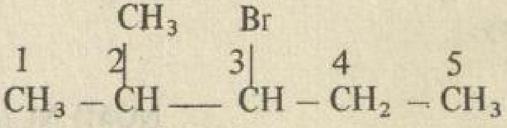
$$\overset{3}{H_3C} - \overset{\overset{Br}{|}}{\overset{2}{C}}H - \overset{1}{CH_3}$$

2-Bromopropane



$$H_3C - \overset{\overset{^1CH_3}{2|}}{\underset{\underset{^3CH_3}{|}}{C}} - Cl$$

2–Chloro-
2–methylpropane



$$\overset{1}{CH_3} - \overset{\overset{CH_3}{2|}}{C}H — \overset{\overset{Br}{3|}}{C}H - \overset{4}{CH_2} - \overset{5}{CH_3}$$

3–Bromo-2-methylpentane

General Methods of Preparation :

1. *From Alcohols.* Alkyl halides are most commonly prepared by the replacement of – OH group in alcohols with halogen by the following methods.

(*a*) Alkyl halides may be prepared by the action of hydrogen halides on alcohols in presence of sulphuric acid or anhydrous zinc chloride.

$$R - O - H + HX \xrightarrow{H_2SO_4} R - X + H_2O$$

This method is generally used for the preparation of tertiary halides.

(*b*) The action of phosphorous halides on an alcohol also gives alky halide . Phosphorus pentahalides (PX_5) as well as phosphorus trihalides (PX_3) can be used in this reaction.

$$ROH + PX_5 \longrightarrow RX + HX + POX_3$$

$$3\,ROX + PX_3 \longrightarrow 3\,RX + \underset{\text{Ortho-phosphorus acid}}{P(OH)_3}$$

Phosphorus tribromide and phosphorus triiodide are commonly used for the preparation of bromo and iodo alkanes.

(*c*) Chloroalkanes may be prepared by refluxing thionylchloride with alcohol in presence of pyridine which acts as a catalyst.

$$ROH + SOCl_2 \longrightarrow RCl + SO_2 + HCl$$

2. *From Alkenes.* Alkyl halides may also be prepared by the addition of halogen acid to alkenes.

$$H_2C = CH_2 + HX \longrightarrow CH_3 - CH_2X$$

3. *From Alkanes.* Haloalkanes may also be obtained by the halogenation of alkanes.

$$R-H + X_2 \longrightarrow R-X + HX$$

General Properties of Monohaloalkanes :

Physical Properties. Due to their higher molecular weights haloalkanes have higher boiling points than their corresponding alkanes. For a given alkyl group, the boiling point increases with the increase of atomic weight of halogen. Haloalkanes are insoluble in water and soluble in organic solvents such as alcohol, ether etc.

Chemical Properties. The important reactions of haloalkanes are those of substitution and elimination. For a given halogen the order of reactivity of haloalkanes is as below :

Ter > Sec. > Primary

For a given alkyl group the order of reactivity of different halides is as below :

Iodide > Bromide > Chloride > Fluoride

Before discussing substitution and elimination in detail we must have some idea about the nature of carbon halogen bond in haloalkanes. The carbon-halogen bond in haloalkanes is a sigma bond formed by the overlap of one [SP^3] hybrid orbital of carbon with the P orbital of the halogen. A pair of electrons is shared between carbon and halogen atom. Unlike inorganic halides, organic halides are covalent compounds and do not have halide ions. Therefore, alkyl halides do not form precipitate of silver halide with silver nitrate. Halogens are more electronegative than carbon. Therefore, shared pair of electrons is not equally distributed between carbon and halogen but is more shifted towards halogen. Thus the electronic cloud of shared pair of electrons is more dense towards halogen than the carbon. Consequently there is a small partial negative charge (δ^-) on the halogen a small partial positive charge (δ^+) on the carbon.

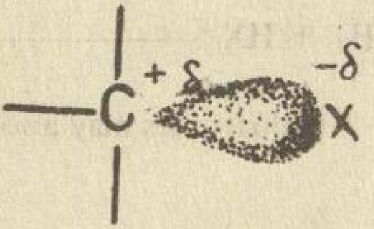


Fig. 15.1

Such a covalent bond in which a pair of electrons is not equally shared but is shifted more towards the more electronegative atom, is called a polarised bond or a polar bond. Thus halogen has induced a partial positive charge to carbon. This is known as inductive effect which is produced due to the difference in the electronegativities of two bound atoms. Due to the partial +ve charge on the carbon atom it acts as an electrophile. While the halogen atom with partial negative charge will have the tendency to be removed as a halide ion (X^-) in a molecule of haloalkane. Therefore, a nucleophile which has a pair of electrons to share with carbon, will attack the carbon to form a new covalent bond and the halogen will be removed as halide ion.

$$Y^- + R - X \longrightarrow R - Y + X^-$$

The nucleophile (Y^-) is called entering group and halogen as the leaving group. The molecule in which substitution takes place is called substrate.

Thus a nucleophile will substitute the halogen and this substitution is known as nucleophilic substitution. A nucleophilic substitution is denoted by (SN) where N stands for nucleophilic and S for substitution.

1. Nucleophilic Substitution (SN) Reactions :

Nucleophilic substitution reactions are very important from synthetic and mechanistic point of view. A large variety of organic compounds can be synthesized by the Nucleophilic substitution of halogen in the haloalkanes. These nucleophiles may be either negativly charged ions such as $\bar{OH}$, $\bar{CN}$, $\bar{NH_2}$, $\bar{OR}$, $\bar{SH}$ or molecules having excess of electronic density as : $\ddot{N}H_3$, $H_2\ddot{O}$; $R\ddot{N}H_2$, $R - \ddot{O} - H$, etc.

R – X + substrate

Nucleophiles	*Compound formed*	*Leaving group*
$\xrightarrow{OH^-}$	$R - OH$ Alcohol	$+ X^-$
$\xrightarrow{OR^-}$	$R - O - R$ Ether	$+ X^-$
$\xrightarrow{CN^-}$	$R - C \equiv N$ Cyanide	$+ X^-$
$\xrightarrow{:NH_3}$	$R - NH_2$ Amine	$+ X^- + H^+$
$\xrightarrow{SH^-}$	$R - SH$ Thioalcohol	$+ X^-$
$\xrightarrow{SR^-}$	$R - S - R$ Thioether	$+ X^-$
$\xrightarrow{\bar{C} \equiv C - H}$	$R - C \equiv C - H$ Alkyne	$+ X^-$

Iodine can replace chlorine and bromine from the respective haloalkanes.

$$R - Br + I^- \longrightarrow R - I + Br^-$$

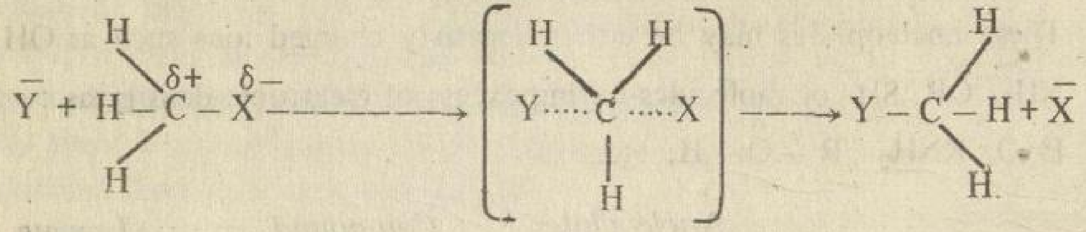
From the above examples the great synthetic importance of nucleophilic substitution reactions of haloalkanes is quite obvious.

Mechanism of Nucleophilic Substitution :

Nucleophilic substitution of a given haloalkane may proceed by one of the following two mechanisms.

(*a*) Bi-molecular Nucleophilic Substitution (SN^2) :

According to this mechanism formation of a new bond between the entering group and electrophilic carbon of haloalkane and breaking of the carbon halogen bond takes place simultaneously. It means that there is a partial bonding between the atom of entering group and electrophilic carbon before carbon – halogen bond is completely broken.



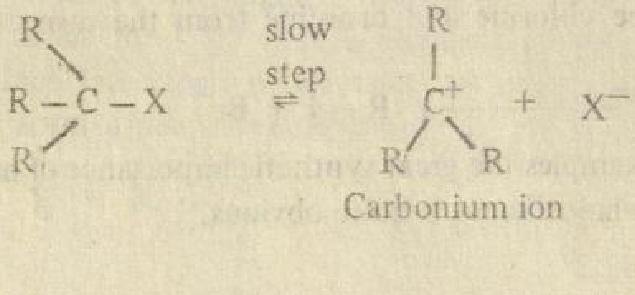
Activated complex

Thus, the reaction is completed in one step. Rate of the reaction can be determined by measuring the rate of this step. Therefore, this step is known as *rate determining step or slow step.* In this rate determining step two types of molecules or two species (attacking nucleophile and haloalkane) are involved in the bond formation and bond breaking. Therefore, this reaction is known as bimolecular reaction. Molecularity of a reaction is defined as the number of species which are involved in the rate determining step of the reaction. Thus this reaction is a bimolecular nucleophilic substitution, which is abbreviated as (SN^2) where 2 stands for bimolecular.

(*b*) Uni-molecular Nucleophilic Substitution (SN^1) :

In this mechanism the reaction is completed in two steps. In the first step carbon-halogen bond is completely broken down giving a carbonium ion and a halide ion.

(*i*)

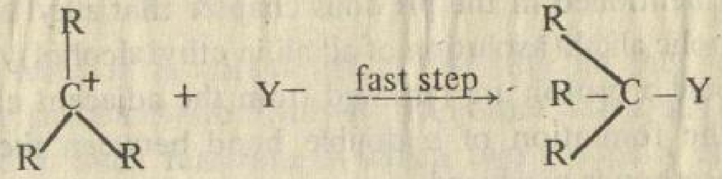


Carbonium ion

In the carbonium ion there are only three groups attached to positively charged carbon. Therefore, carbonium ion has a planar structure with an angle of 120° between any two bonds.

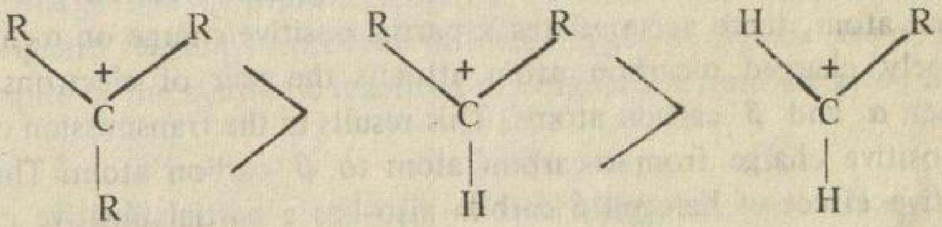
In the second step carbonium ion is attacked by the nucleophile and the new covalent bond is formed between the nucleophile and carbon.

(*ii*)



In the first step breaking of covalent bond takes place which is an energy consuming process. In the second step a new covalent bond is formed which is an energy liberating process. Therefore the first step is slow and the second step is fast. Thus the rate of reaction will depend upon the first step which is the rate determining step. Since in this mechanism only one molecule is involved in the rate determining step, therefore, this reaction is unimolecular nucleophilic substitution and is represented by SN^1 where '1' stands for unimolecular.

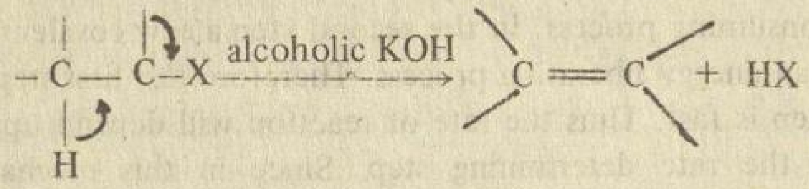
SN^1 mechanism involves the formation of carbonium ion in rate determining step. The ease of formation of carbonium ion will depend upon its relative stability. As pointed out earlier tertiary carbonium ions are more stable than secondary carbonium ions and in turn secondary carbonium ions are more stable than primary carbonium ions.



Alkyl group attached to the positively charged carbon decreases the magnitude of positve charge on carbon and thus stabilizes the carbonium ion. Therefore, greater the number of alkyl groups attached to the positively charged carbon, greater is the stability of carbonium ion. This is one of the important reasons that tertiary halides undergo nucleophilic substitution by SN^1 mechanism. While the nucleophilic substitution of primary halides generally proceeds through SN^2 mechanism. Nucleophilic substitution of secondary halides may proceed either through SN^1 or SN^2 mechanism depending on the conditions of reactions and structure of the substrate. Increase in the polarity of solvent favours SN^1 mechanism.

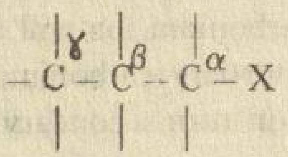
2. Elimination Reactions :

It has been mentioned in the previous chapter that alkyl halides, when treated with ethanolic alkali(a solution of alkali in ethyl alcohol)yield alkenes. A halogen anion and a proton are removed from the adjacent carbon atoms which result in the formation of a double bond between them. Thus an unsaturated hydrocarbon is produced.

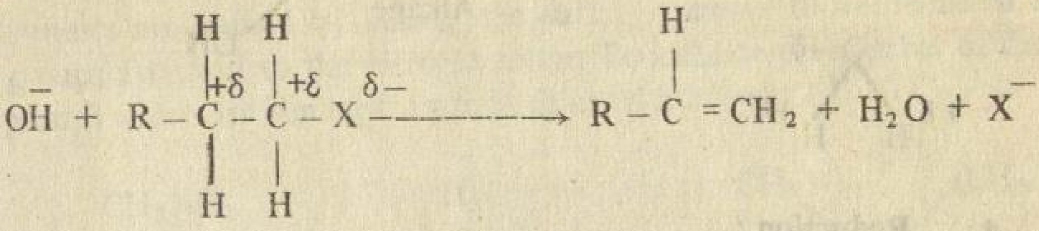


The reaction is known as elimination.

The carbon to which a halogen atom is attached is referred as α-carbon atom and the carbon adjacent to α-carbon is called as β carbon atom and so on.



As pointed out earlier that because of greater electronegativity of the halogen atom, there accumulates a partial positive charge on α-carbon. The positively charged α-carbon atom attracts the pair of electrons which is between α and β carbon atoms. This results in the transmission of some of the positive charge from α-carbon atom to -β -carbon atom. Thus due to inductive effect of halogen β carbon also has a partial positive charge but smaller than that on α-carbon. Consequently carbon-hydrogen bond of β-carbon also becomes polarized and hydrogen attached to β-carbon acquires a small positve charge. In this way hydrogen or hydrogens attached to β-carbon become acidic and can be eliminated in the form of proton in presence of strong bases. On the other hand halogen being partially negatively charged has the tendency to be detached as halide ion. Therefore, in the presence of an alkali a β-carbon will lose a proton and from the α-carbon halogen will be eliminated as halide ion. This will result in the formation of a double bond between α and β-carbons.



$$\overset{-}{OH} + R-\underset{H}{\overset{H}{\overset{+\delta}{C}}}-\underset{H}{\overset{H}{\overset{+\delta}{C}}}-\overset{\delta-}{X} \longrightarrow R-\overset{H}{C}=CH_2 + H_2O + \overset{-}{X}$$

This reaction is completed in one step. In this reaction two species (haloalkane and base) are involved. Therefore, it is a bimolecular elimination reaction (E^2). Such reactions in which two groups or atoms are eliminated from two adjacent carbons, are called β-elimination reactions.

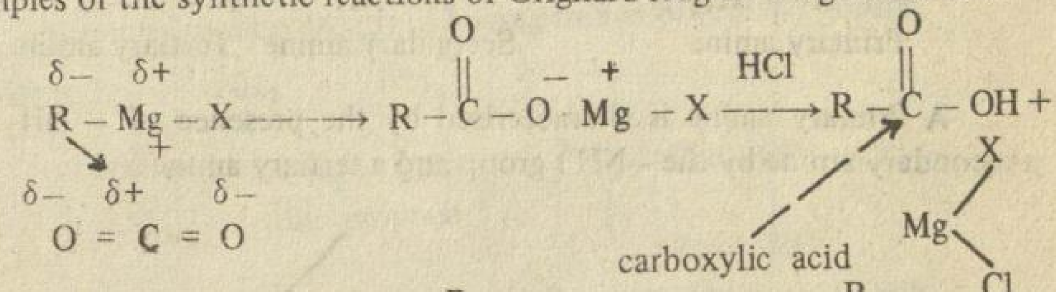
3. Reaction with Magnesium :–

An ethereal solution of alkyl halide reacts with magnesium to form alkyl magnesium halide known as Grignard Reagent. Ether should be free from traces of water.

$$RX + Mg \xrightarrow{\text{ether}} \overset{\delta-}{R} - \overset{\delta+}{Mg} - X$$

Grignard reagent was first introduced by Grignard in 1900. Grignard reagents have a great synthetic importance as a large number of different types of organic compounds can be synthesised from these reagents. In Grignard reagent carbon attached to magnesium is more electronegative than magnesium. Therefore, alkyl group attached to magnesium has partial negative charge and is thus nucleophilic in nature. Different electrophiles attack Grignard reagent to produce different types of organic compounds. A few examples of the synthetic reactions of Grignard reagent are given below:

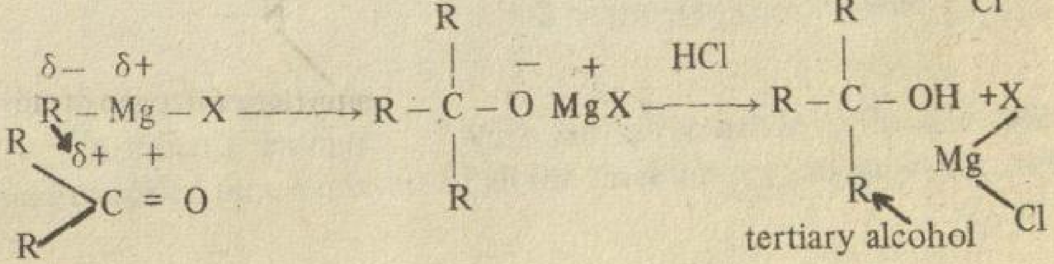
(*i*)



$$\overset{\delta-}{R}-\overset{\delta+}{Mg}-X + \overset{\delta-}{O}=\overset{\delta+}{C}=\overset{\delta-}{O} \longrightarrow R-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\ \overset{+}{Mg}-X \xrightarrow{HCl} R-\overset{O}{\overset{\|}{C}}-OH + X-Mg-Cl$$

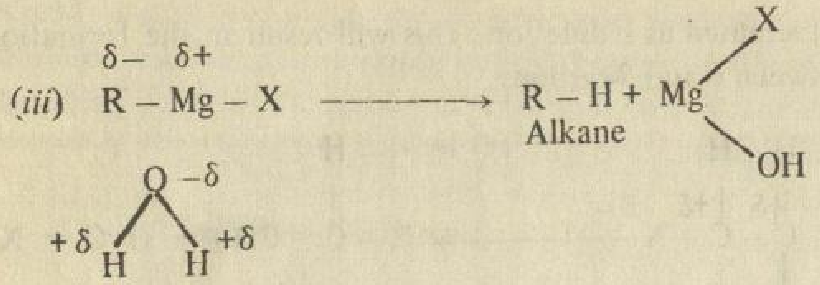
carboxylic acid

(*ii*)



$$\overset{\delta-}{R}-\overset{\delta+}{Mg}-X + \begin{matrix}R\\ \\R\end{matrix}\!\!>\overset{\delta+}{C}=O \longrightarrow R-\underset{R}{\overset{R}{C}}-\overset{-}{O}\ \overset{+}{Mg}X \xrightarrow{HCl} R-\underset{R}{\overset{R}{C}}-OH + X-Mg-Cl$$

tertiary alcohol



4. **Reduction :**

With nascent hydrogen (Sn and HCl), haloalkanes are reduced to form alkanes.

$$R-X + 2\,[H] \xrightarrow{Sn/HCl} RH + HX$$

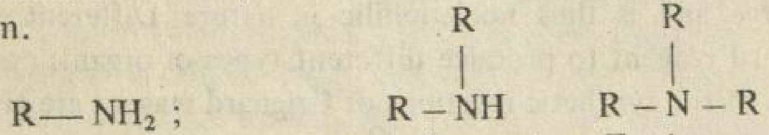
5. **Wurtz Reaction**

An ethereal solution of alkyl halide on treatment with sodium or zinc yield alkane, *e.g.*

$$2R-X + 2Na \longrightarrow R-R + 2NaX$$

ALIPHATIC AMINES

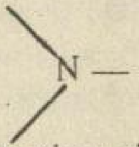
Amines are derived from ammonia by the replacement of one or more hydrogen atoms by alkyl groups. They are classified into primary, secondary and tertiary amines according to the number of alkyl groups attached to the nitrogen atom.



$$R-NH_2 \;;\qquad R-\underset{}{\overset{\displaystyle R\atop |}{N}}H \qquad R-\overset{\displaystyle R\atop |}{N}-R$$

Primary amine Secondary amine Tertiary amine

A Primary amine is characterised by the presence of $-NH_2$ group, a secondary amine by the $-\underset{|}{N}H$ group and a tertiary amine by

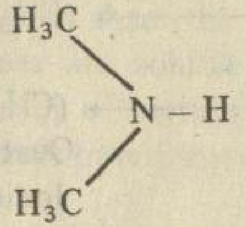


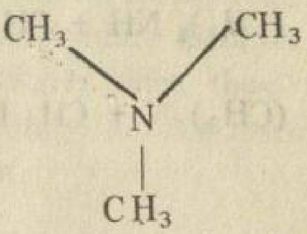
a tertiary nitrogen atom

Nomenclature :

Amines are named by adding the suffix – *amine* to the name of the alkyl groups attached to the nitrogen atom. To indicate the number of those alkyl groups which are similar the prefix di or tri is added.

CH_3NH_2
methylamine

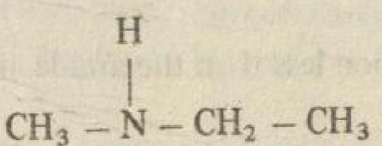

Dimethylamine

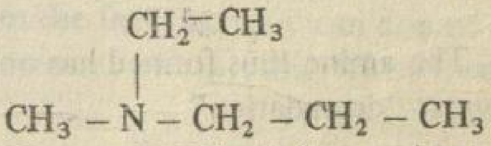

Trimethylamine

When all the alkyl groups are the same, amines are called simple and when different they are called mixed amines.

To name the amines with different alkyl groups they are considered to be N-alkyl substituted derivatives of primary amines. For naming the parent primary amine the largest alkyl group is chosen. To indicate the substitution of alkyl groups on nitrogen, N-is prefixed before the name of the substituent group.

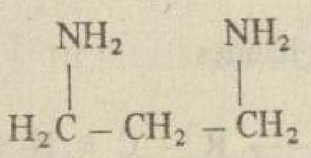
Examples:

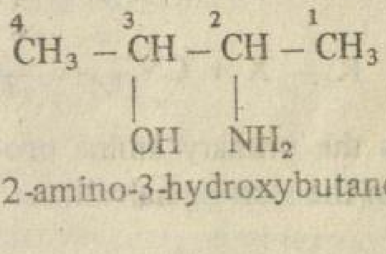

$$CH_3-\overset{\overset{\displaystyle H}{|}}{N}-CH_2-CH_3$$
N – methyl-ethyl amine


$$CH_3-\overset{\overset{\displaystyle CH_2-CH_3}{|}}{N}-CH_2-CH_2-CH_3$$
N – methyl-N-ethyl-propylamine

The IUPAC system is not in general use for the nomenclature of simple amines. However, it is preferred for naming the complex amines such as those having two or more amino groups or having mixed functional groups.

Examples :


$$\overset{\overset{\displaystyle NH_2}{|}}{H_2C}-CH_2-\overset{\overset{\displaystyle NH_2}{|}}{CH_2}$$
1, 3-diamino propane


$$\overset{4}{C}H_3-\underset{\underset{\displaystyle OH}{|}}{\overset{3}{C}H}-\underset{\underset{\displaystyle NH_2}{|}}{\overset{2}{C}H}-\overset{1}{C}H_3$$
2-amino-3-hydroxybutane

General Methods of Preparation :

1. *Hoffman's method* : When an alkyl halide is heated with ammonia in a sealed tube a mixture of all the three amines (primary , sec. and

ter.) along with, quaternary ammonium compound is obtained.

$$\overset{\delta+}{CH_3}-\overset{\delta-}{I}+\overset{\delta+}{H}-\ddot{N}H_2 \longrightarrow CH_3-\ddot{N}H_2+HI$$

$$CH_3\ddot{N}H_2 + CH_3I \longrightarrow (CH_3)_2\ddot{N}H + HI$$

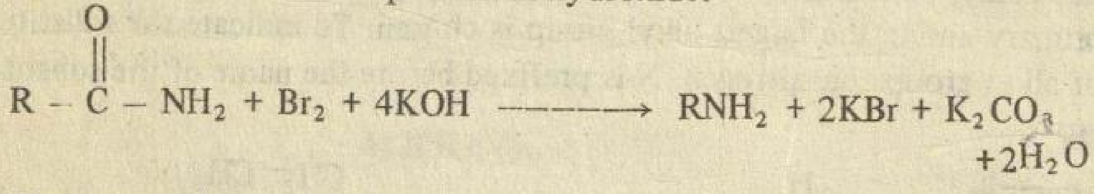
$$(CH_3)_2\ddot{N}H + CH_3I \longrightarrow (CH_3)_3\ddot{N} + HI$$

$$(CH_3)_3\ddot{N} + CH_3I \longrightarrow (CH_3)_4\overset{+}{N}I^-$$

Quaternary Ammonium Iodide

A large excess of ammonia gives a good yield of primary amine while excess of alkyl halide gives tertiary amine as the principal product.

2. *By Hoffmann Degradation (Hypobromite method)* : Acid amides ($R-\overset{\overset{O}{\|}}{C}-NH_2$) can be converted into primary amines by treating them with bromine and hot concentrated potassium hydroxide.



$$R-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4KOH \longrightarrow RNH_2 + 2KBr + K_2CO_3 + 2H_2O$$

The amine thus formed has one carbon less than the amide and hence is known as "degradation"

3. *By reduction of Nitriles* : Nitriles are reduced to primary amines by H_2 in the presence of some catalyst such as Nickel.

$$R-C\equiv N \xrightarrow{H_2/Ni} R-CH_2-NH_2$$

Nitriles can be obtained easily from alkyl halides

$$R-X + CN^- \longrightarrow R-C\equiv N + X^-$$

Thus the primary amine produced by this method contains one more carbon than the starting haloalkane.

4. *By the reduction of Nitro alkanes* : Nitroalkanes ($R - NO_2$) are reduced to primary amines by a metal and an acid or by catalytic hydrogenation.

$$R - NO_2 + 6H \xrightarrow[\text{or Metal/acid.}]{H_2 / Pt} R - NH_2 + 2H_2O$$

General Properties of amines :

Physical Properties : Most of the common amines are liquids. Their boiling points are generally higher than the corresponding alcohols and carboxylic acids. Smaller amines are soluble in water since they form hydrogen bonds with water. Smell of methyl and ethyl amines resembles that of ammonia while higher amines have fishy odour.

Chemical Properties :

The nitrogen atom in an amine molecule is sp^3 hybridized. Three sp^3 orbitals of the nitrogen atom are partially filled and can overlap with the partially filled orbitals of other atoms to form NH_3, NH_2R, NHR_2 or NR_3. The fourth sp^3 orbital is filled with an electron pair and is not used in bond formation. Thus ammonia and alkyl amines have tetrahedral geometry. The unshared pair of electrons is shown with two dots on nitrogen in ordinary structural formulas :

$$R - \ddot{N}H_2$$

1. *Basic Properties :* Like ammonia amines also show basic properties. Their basic character arises from the fact that they can donate the lone pairs of electrons located on "N" – atom to a proton, When treated with acids.

$$R - \ddot{N}H_2 + HX \longrightarrow R - \overset{+}{N}H_3\ \overset{-}{X}$$

Being basic , amines can form salts with acids.

$$CH_3\ddot{N}H_2 + HCl \longrightarrow CH_3\overset{+}{N}H_3\overset{-}{Cl}$$

$$(CH_3)_2\ddot{N}H + HCl \longrightarrow (CH_3)_2\overset{+}{N}H_2\overset{-}{Cl}$$

$$(CH_3)_3\ddot{N} + HCl \longrightarrow (CH_3)_3\ \overset{+}{N}H\overset{-}{Cl}$$

2. *Reactions with Nitrous Acid :* Primary and secondary amines react with HNO_2 to yield an alcohol and a nitroso compound respectively.

$$CH_3 - NH_2 + HNO_2 \longrightarrow CH_3OH + N_2 + H_2O$$

Methyl amine
(Primary amine)

$$(CH_3)_2NH + HONO \longrightarrow (CH_3)_2N-N=O + H_2O$$

Secondary amine dimethyl nitroso amine

Tertiary amines form salts with nitrous acid

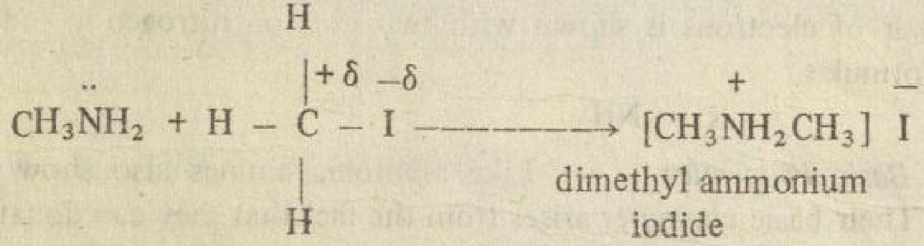
$$R_3N: + HNO_2 \longrightarrow \overset{+}{[R_3NH]}\,\overset{-}{NO_2}$$

Tertiary amine Trialkyl ammonium nitrite

This reaction of aliphatic amines can be used to distinguish between the three classes of amines.

3. *Alkylation* : There is a lone pair of electrons on the N-atom of the amines and hence they can act as nucleophilés.

Amines and alkyl halides react together to give the alkyl derivatives of the amines. The first step of the reaction is a Nucleophilic substitution on the carbon atom of the alkyl halide.



$$CH_3\ddot{N}H_2 + H-\underset{H}{\overset{H}{\overset{+\delta}{C}}}-\overset{-\delta}{I} \longrightarrow \overset{+}{[CH_3NH_2CH_3]}\ \overset{-}{I}$$

dimethyl ammonium iodide

The dimethyl ammonium iodide, which is an acid, can donate a proton to base or to the excess of Primary amine to liberate a secondary amine.

$$CH_3-\overset{+}{N}H_2-CH_3 \xrightarrow[-\overset{+}{H}]{B:} (CH_3)_2NH + \overset{+}{B}H$$

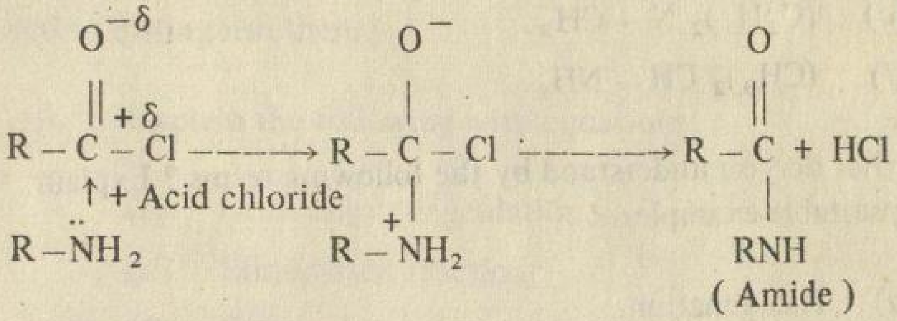
The secondary amine thus formed undergoes a similar reaction with alkyl halide to yield a tertiary amine which in turn gives, on similar treatment a quarternary ammonium ion. Therefore in this reaction a mixture of products is formed.

$$CH_3NH_2 + CH_3I \longrightarrow (CH_3)_2NH + HI$$

$$(CH_3)_2NH + CH_3I \longrightarrow (CH_3)_3N + HI$$

$$(CH_3)_3\ddot{N} + CH_3I \longrightarrow (CH_3)_3\overset{+}{N}-CH_3 + \overset{-}{I}$$

4. *Acylation :* Primary and secondary, but not the tertiary amines react with acid chlorides or acid anhydrides. In these reactions a hydrogen atom in the NH_2 group or NH group is replaced by an acyl group $(R-\overset{\overset{O}{\|}}{C}-)$. Therefore, this reaction is called acylation. The lone pair of electrons on nitrogen is donated to the electrophilic carbon of acyl group.



5. *Carbyl amine Reaction :* Primary amines on warming with chloroform and an alcoholic solution of Potassium hydroxide give isonitriles (isocyanides or carbylamines), which have extraordinarily disagreeable odour and are poisonous.

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow R-NC + 3KCl + 3H_2O$$

This reaction is given only by primary amines and is used as a test for primary amines.

QUESTIONS

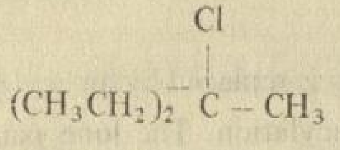
1. Write structural formulae for each of the following substances:

   (*a*) 1, 1, 1 – Trichloropropane.
   (*b*) Tertiary butyl chloride.
   (*c*) n-butyl iodide
   (*d*) Methyl ethyl amine.
   (*e*) Isopropyl amine.

2. Suggest a name for the following compounds:

   (*a*) $CH_3CH{-}Br(CH_2)_2 - CH_3$

(*b*) $CH_3CHBr-CH(CH_3).CH_2CH_2I.$

(*c*) 

$(CH_3CH_2)_2C(Cl)-CH_3$

(*d*) $(CH_3)_3N.$

(*e*) $(C_2H_5)_2N-CH_3.$

(*f*) $(CH_3)_2CH-NH_2.$

3. What do you understand by the following terms ? Explain your answer giving suitable examples.

(*a*) Halogenation.

(*b*) Dehydrohalogenation.

(*c*) Alkylation.

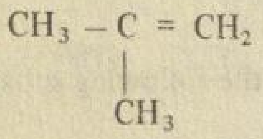
(*d*) Acylation.

(*e*) Amination.

4. What is Markownikoff's rule ?

What addition products would you get when hydrogen chloride is added in the following :

(*i*) $CH_3-CH=CH_2$

(*ii*) 

$CH_3-C(CH_3)=CH_2$

(*iii*) $CH_2=CH-CH_2-CH_3.$

5. What is nucleophilic substitution ? Give examples.

6. What do you mean by primary, secondary and tertiary halides and amines ? Illustrate with examples.

7. Write an equation for the preparation of the following compounds by a displacement reaction on alkyl halide :

(*a*) n-propyl alcohol.

(*b*) n-butyl cyanide.

(*c*) ethyl amine.

(*d*) methyl ethyl ether.

(*e*) 2-butyne.

8. Propyl amine, methyl – ethyl amine, and trimethyl amine have the same molecular formula. Show how the reaction with nitrous acid could be used to distinguish them.

9. Explain the following with equations.

(*i*) Hoffmann's degradation.

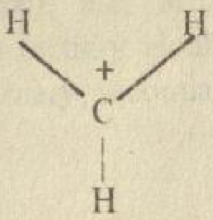
(*ii*) Elimination reaction.

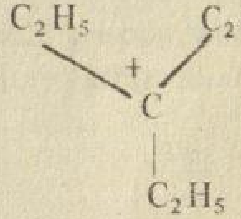
(*iii*) Grignard reaction.

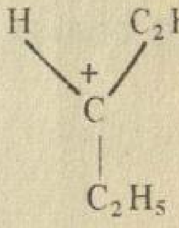
(*iv*) Carbyl-amine reaction.

(*v*) Wurtz reaction.

10. (*a*) Arrange the following carbonium ions in the increasing order of their stability:





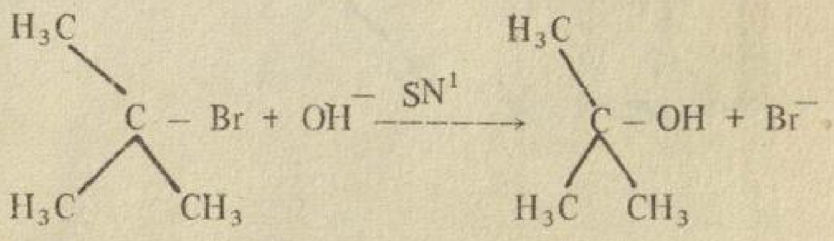


(*b*) What do you understand by SN^1 , SN^2 mechanisms and molecularity of a reaction ?

11. Write the mechanisms of the following reactions :

(*i*) $CH_3 - Br + I^- \xrightarrow{SN^2} CH_3I + Br^-$

(*ii*)

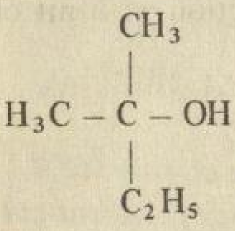


$(H_3C)_2(CH_3)C - Br + OH^- \xrightarrow{SN^1} (H_3C)_2(CH_3)C - OH + Br^-$

12. What is β-elimination ? Write the chemical equations for the action of alcoholic potassium hydroxide on 1-chloropropane. Give the mechanism of the reaction.

13. How are Grignard's reagent prepared ?

How will you obtain (*i*) CH_3CH_2COOH (*ii*) C_2H_6 &

(*iii*) 

$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle C_2H_5}{|}}{C}}-OH$$

from C_2H_5MgBr.

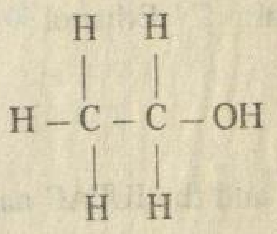
CHAPTER 16

ALCOHOLS AND ETHERS

Aliphatic organic compounds having one or more hydroxy groups (–OH) attached to carbon are called alcohols. Alcohols constitute an important homologous series. Alcohols having one hydroxy group per molecule are called polyhydric alcohols. Polyhydric alcohols can be further divided into dihydric (containing two hydroxy groups), trihydric alcohols (with three hydroxy groups), etc. Monohydric alcohols are classified into primary, secondary and tertiary alcohols depending upon whether hydroxy group is attached to primary, secondary or tertiary carbon atom.

Examples :

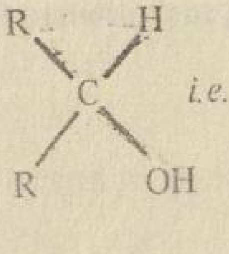
Primary alcohols, $R-CH_2-OH$ i.e.,



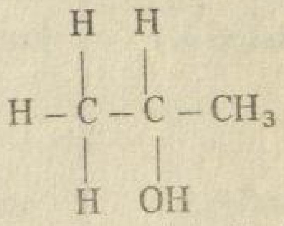
$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & - & C & -OH \\ & | & & | & \\ & H & & H & \end{array}$$

ethyl alcohol

Secondary alcohol.

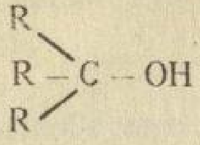
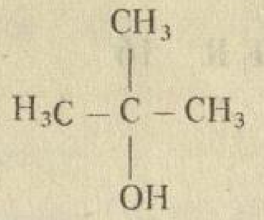


i.e.



$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & - & C & -CH_3 \\ & | & & | & \\ & H & & OH & \end{array}$$

Sec. Propyl alcohol

Tertiary alcohol,  *i.e.* , 

$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}-CH_3$$

Ter. Butyl alcohol

Nomenclature :

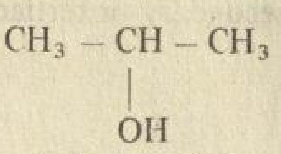
1. *Common System* : Alcohol having five or less than five carbon atoms are generally known by their common names. In this system the name of the alkyl group is followed by the separate word "alcohol". The prefixes pri, sec ter. are used to indicate primary, secondary, and tertiary alcohols.

CH_3-OH	CH_3-CH_2-OH
Methyl alcohol	Ethyl alcohol

2. *IUPAC System* : The longest continuous carbon chain containing hydroxy group is selected. From the name of corresponding alkane the ending – e is replaced by the ending – ol. Position number of hydroxy group is placed before the modified name of the alkane. For naming polyhydric alcohols ending – diol, triol, etc. are added after the name of the parent hydrocarbon.

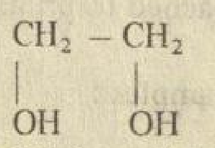
CH_3OH Methanol

CH_3CH_2OH Ethanol



$$CH_3-\underset{\displaystyle OH}{CH}-CH_3$$

2 - Propanol



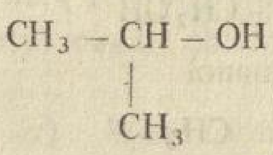
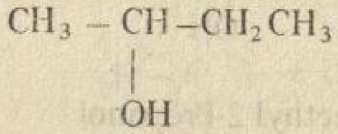
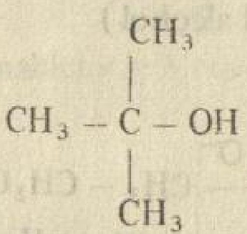
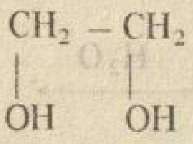
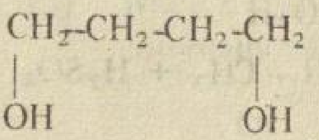
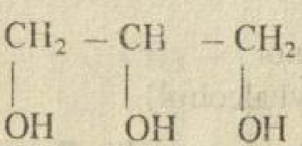
$$\underset{\displaystyle OH}{CH_2}-\underset{\displaystyle OH}{CH_2}$$

1,2-Ethanediol

The common and the IUPAC names of a few alcohols are given in Table 16.1.

TABLE 16.1

Alcohols and their Common and IUPAC names :

	Formula	Common name	IUPAC
1.	CH_3OH	Methyl alcohol	Methanol
2.	CH_3CH_2OH	Ethyl alcohol	Ethanol
3.	$CH_3CH_2CH_2OH$	Propyl alcohol	1 - Propanol
4.	 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-OH$	Sec. Propyl alcohol	2 -Propanol
5.	$CH_3CH_2CH_2CH_2OH$	n. Butyl alcohol	1 - Butanol
6.	 $CH_3-\underset{\underset{OH}{\vert}}{CH}-CH_2CH_3$	Sec. Butyl alcohol	2 - Butanol
7.	 $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-OH$	ter. Butyl alcohol	2 - methyl-2-Propanol
8.	 $\underset{\underset{OH}{\vert}}{CH_2}-\underset{\underset{OH}{\vert}}{CH_2}$	Ethylene glycol	1,2-Ethanediol
9.	 $\underset{\underset{OH}{\vert}}{CH_2}-CH_2-CH_2-\underset{\underset{OH}{\vert}}{CH_2}$	Tetramethylene glycol	1,4-Butanediol
10.	 $\underset{\underset{OH}{\vert}}{CH_2}-\underset{\underset{OH}{\vert}}{CH}-\underset{\underset{OH}{\vert}}{CH_2}$	Glycerol or glycerine	1,2,3-Propanetriol

GENERAL METHODS OF PREPARATION

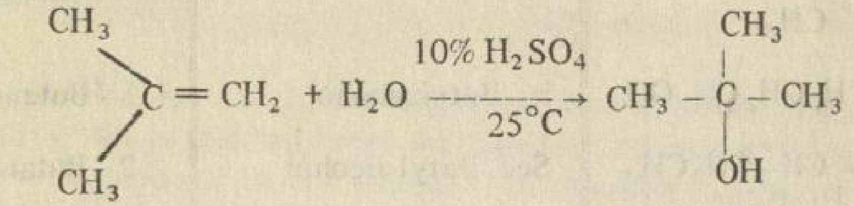
Preparation :

1. **From Alkenes** :– Some alcohols like ethyl alcohol, isopropyl alcohol, sec-butyl and ter-butyl alcohols are obtained commercially by the hydration of alkenes. Alkenes can be hydrated into alcohols by two methods (*i*) By the direct addition of water to double bond in the presence of dil H_2SO_4 . (*ii*) By treating the alkenes with conc. H_2SO_4 followed by hydrolysis of alkyl hydrogen sulphate into alcohol.

(*i*) **Direct Addition of Water :**

$$H_2C = CH_2 + H_2O \xrightarrow[240^\circ C]{10\%\ H_2SO_4} H_3C - CH_2OH$$

Ethene Ethanol

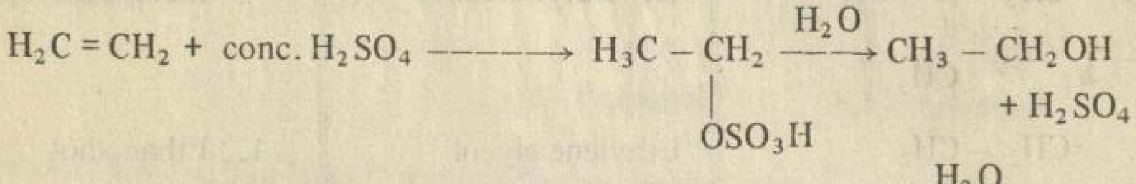


$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C = CH_2 + H_2O \xrightarrow[25^\circ C]{10\%\ H_2SO_4} CH_3 - \overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}} - CH_3$$

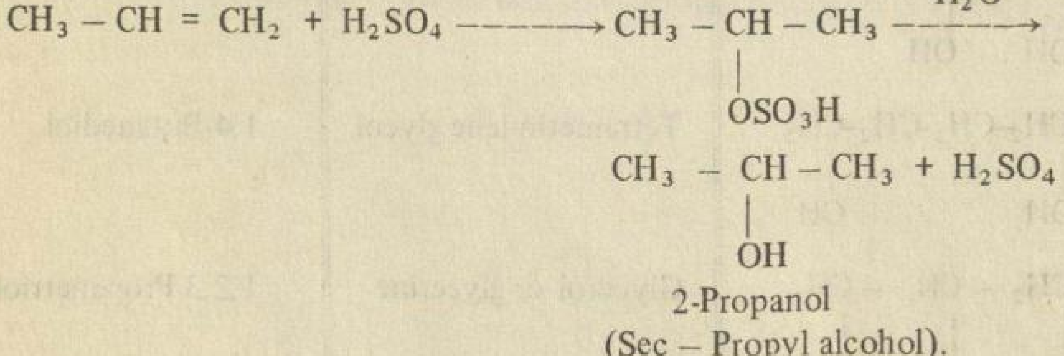
2- methyl propene

2-methyl 2-Propanol
(ter-butyl alcohol)

(*ii*) **With Conc. Sulphuric Acid and Hydrolysis :**



$$H_2C = CH_2 + \text{conc. } H_2SO_4 \longrightarrow H_3C - \underset{\displaystyle OSO_3H}{CH_2} \xrightarrow{H_2O} CH_3 - CH_2OH + H_2SO_4$$



$$CH_3 - CH = CH_2 + H_2SO_4 \longrightarrow CH_3 - \underset{\displaystyle OSO_3H}{CH} - CH_3 \xrightarrow{H_2O} CH_3 - \underset{\displaystyle OH}{CH} - CH_3 + H_2SO_4$$

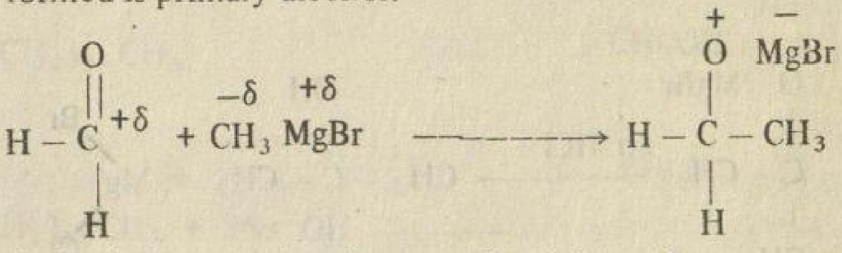
2-Propanol
(Sec – Propyl alcohol).

2. **Reaction of Carbonyl Compounds with Organometallic Reagents:** This method is of particular importance because it allows the formation of

nearly every kind of alcohol. Organic compounds containing carbonyl group ($C = O$) are called carbonyl compounds such as aldehyde ($R - \overset{\overset{O}{\|}}{C} - H$), ketones ($R - \overset{\overset{O}{\|}}{C} - R$), esters ($R - \overset{\overset{O}{\|}}{C} - O - R$), etc.

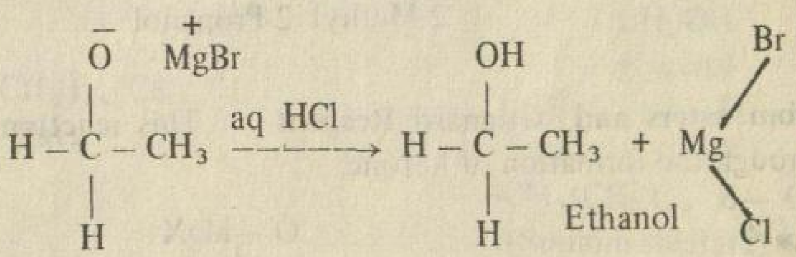
The carbonyl compounds react with organometallic compounds (Compounds having a metal atom directly linked with carbon) to form alcohols. The alcohol formed is more complex than the starting material. The organometallic compounds most frequently used for this purpose are Grignard reagents ($R - Mg - X$). Different types of alcohols (primary, secondary or tertiary) may be obtained by using different kinds of carbonyl compounds.

(*a*) When formaldehyde is used as the starting material the compound formed is primary alcohol.



$$H-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{C}}{}^{+\delta} + \overset{-\delta}{CH_3}\ \overset{+\delta}{MgBr} \longrightarrow H-\underset{\underset{H}{|}}{\overset{\overset{\overset{+\qquad -}{O\quad MgBr}}{|}}{C}}-CH_3$$

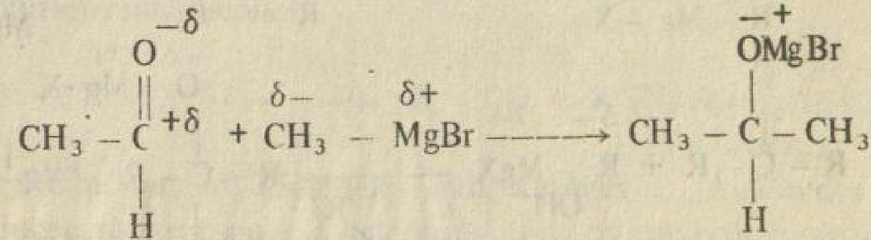
Formaldehyde Methyl magnesium (Intermediate) Bromide



$$H-\underset{\underset{H}{|}}{\overset{\overset{\overset{-\qquad +}{\bar{O}\quad MgBr}}{|}}{C}}-CH_3 \xrightarrow{\text{aq HCl}} H-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 + Mg\begin{matrix}\diagup Br\\ \diagdown Cl\end{matrix}$$

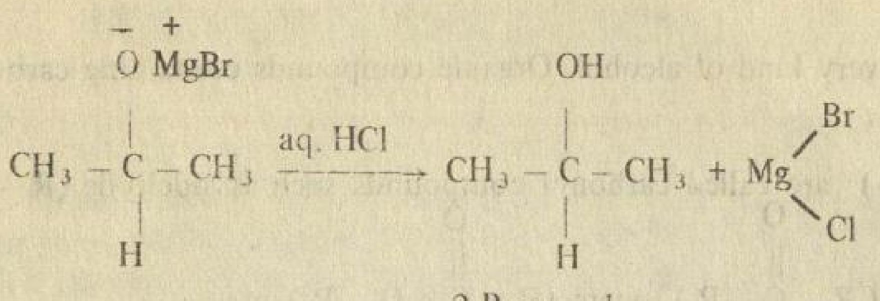
Ethanol

(*b*) When aldehydes other than formaldehydes are used the compounds formed are Secondary alcohol, *e.g.*



$$CH_3-\underset{\underset{H}{|}}{\overset{\overset{O^{-\delta}}{\|}}{C}}{}^{+\delta} + \overset{\delta-}{CH_3} - \overset{\delta+}{MgBr} \longrightarrow CH_3-\underset{\underset{H}{|}}{\overset{\overset{\overset{-+}{OMgBr}}{|}}{C}}-CH_3$$

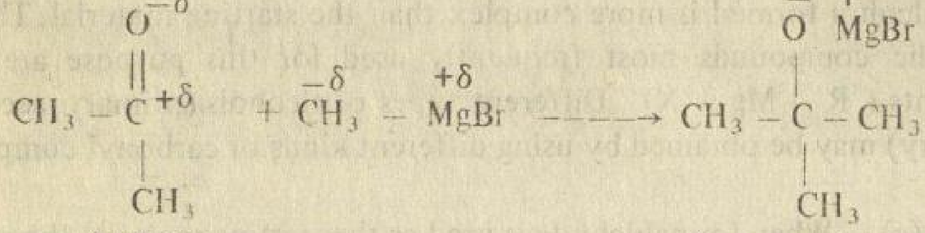
Acetaldehyde Methyl magnesium Bromide (Intermediate)



$$CH_3-\underset{H}{\overset{\overset{-}{O}\,\overset{+}{MgBr}}{C}}-CH_3 \xrightarrow{aq.\ HCl} CH_3-\underset{H}{\overset{OH}{C}}-CH_3 + Mg\begin{smallmatrix}Br\\Cl\end{smallmatrix}$$

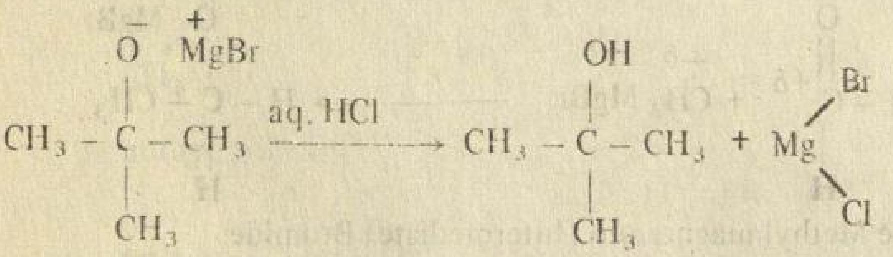
2-Propanol

(*c*) With a ketone the product is a tertiary alcohol.



$$CH_3-\underset{CH_3}{\overset{O^{-\delta}}{\overset{\|}{C}}}{}^{+\delta} + \overset{-\delta}{CH_3}-\overset{+\delta}{MgBr} \longrightarrow CH_3-\underset{CH_3}{\overset{\overset{-}{O}\ \overset{+}{MgBr}}{C}}-CH_3$$

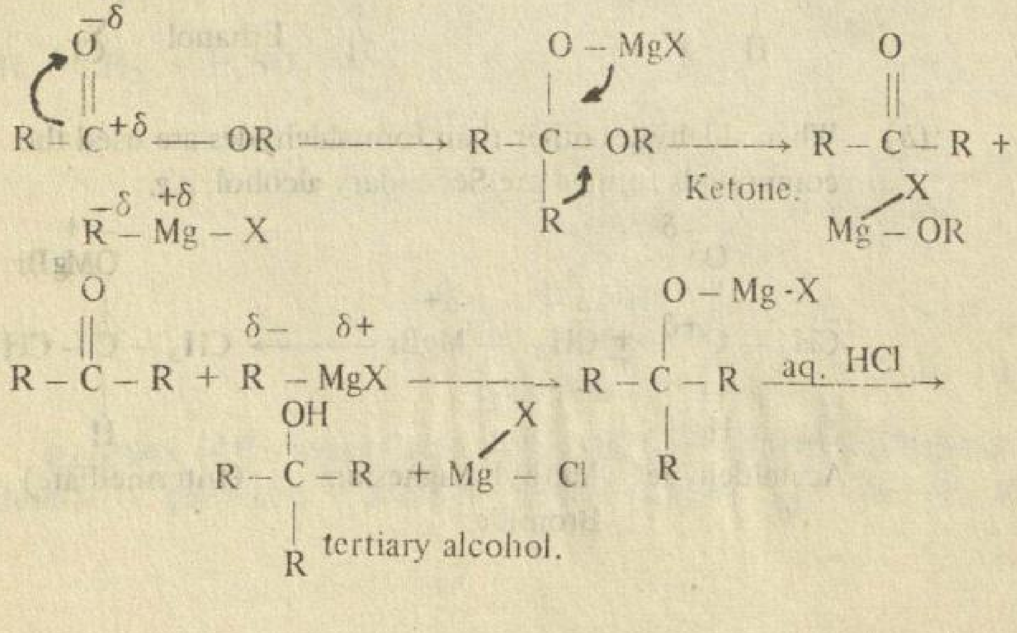
Acetone (Intermediate)



$$CH_3-\underset{CH_3}{\overset{\overset{-}{O}\ \overset{+}{MgBr}}{C}}-CH_3 \xrightarrow{aq.\ HCl} CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_3 + Mg\begin{smallmatrix}Br\\Cl\end{smallmatrix}$$

2-Methyl 2-Propanol

(*d*) **From esters and Grignard Reagent :** This reaction proceeds through the formation of ketone



$$\underset{\overset{-\delta}{R}-\overset{+\delta}{Mg}-X}{R-\overset{\overset{-\delta}{O}}{\overset{\|}{C}}{}^{+\delta}-OR} \longrightarrow R-\underset{R}{\overset{O-MgX}{C}}-OR \longrightarrow \underset{\text{Ketone.}}{R-\overset{O}{\overset{\|}{C}}-R} + Mg\begin{smallmatrix}X\\OR\end{smallmatrix}$$

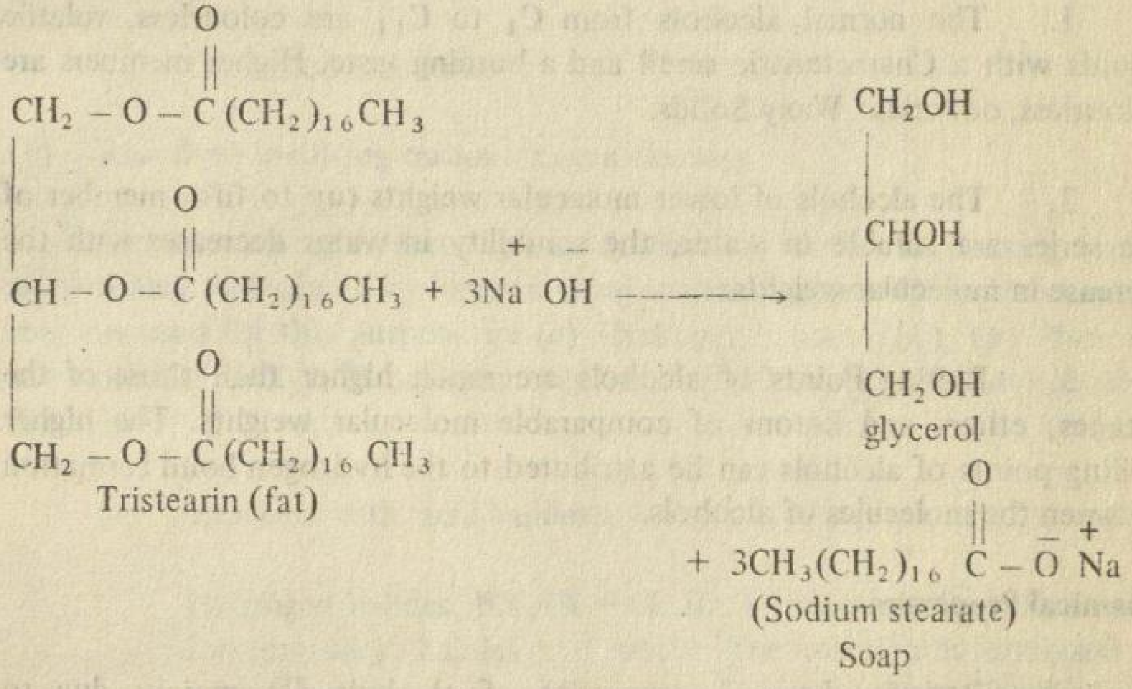
$$R-\overset{O}{\overset{\|}{C}}-R + \overset{\delta-}{R}-\overset{\delta+}{MgX} \longrightarrow R-\underset{R}{\overset{O-Mg-X}{C}}-R \xrightarrow{aq.\ HCl} R-\underset{R}{\overset{OH}{C}}-R + Mg\begin{smallmatrix}X\\Cl\end{smallmatrix}$$

tertiary alcohol.

3. **Hydrolysis of Esters :** Esters ($R - \overset{\overset{\displaystyle O}{\|}}{C} - OR$) are formed when carboxylic acids react with alcohols. They are hydrolysed by aq. solutions of sodium or potassium hydroxide to produce alcohol and acid.

$$R - \overset{\overset{\displaystyle O}{\|}}{C} - OR + NaOH \longrightarrow R - \overset{\overset{\displaystyle O}{\|}}{C} - \overset{-}{O}\ \overset{+}{Na} + R - OH$$

A number of alcohols can be obtained by the hydrolysis of naturally occuring esters. Oils and fats are the naturally occuring esters of glycerol with higher fatty acids like stearic acid, oleic acid, or palmitic acid. Oils or fats when hydrolysed in presence of sodium hydroxide or Potassium hydroxide, produce glycerol and soaps. The latter are sodium or Potassium salts of the higher fatty acids. Because of the soap formation the alkaline hydrolysis of esters is often referred to as *Saponification*.

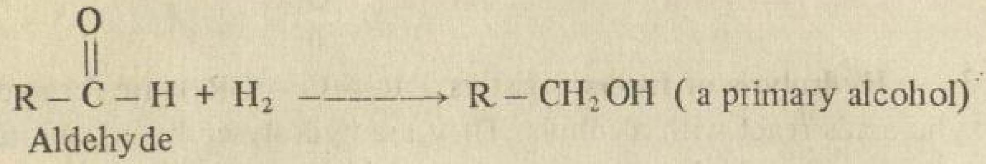


$$\begin{array}{l} CH_2 - O - \overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_{16}CH_3 \\ | \\ CH - O - \overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_{16}CH_3 \\ | \\ CH_2 - O - \overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_{16}CH_3 \end{array} + 3\overset{+}{Na}\ \overset{-}{OH} \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3CH_3(CH_2)_{16}\overset{\overset{\displaystyle O}{\|}}{C} - \overset{-}{O}\ \overset{+}{Na}$$

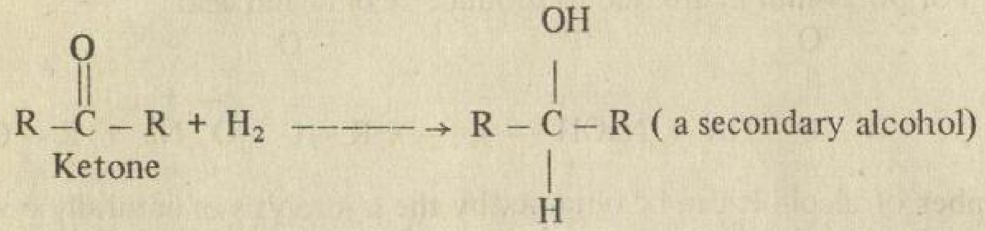
4. **By Hydrolysis of Haloalkanes :** Haloalkanes can be hydrolysed in weakly basic solutions into alcohols.

$$HO^- + \overset{\delta+}{R} - \overset{\delta-}{X} \longrightarrow R - OH + X^-$$ (Nucleophilic substitution).

5. **By Reduction of Aldehydes and Ketones :** Aldehydes and ketones are reduced to corresponding alcohols either by catalytic hydrogenation or by lithium aluminium hydride ($LiAlH_4$). Aldehydes on reduction yield primary alcohols and ketones on reduction give secondary alcohols.



$$\underset{\text{Aldehyde}}{R-\overset{\overset{\large O}{\|}}{C}-H} + H_2 \longrightarrow R-CH_2OH \text{ (a primary alcohol)}$$



$$\underset{\text{Ketone}}{R-\overset{\overset{\large O}{\|}}{C}-R} + H_2 \longrightarrow R-\overset{\overset{\large OH}{|}}{\underset{\underset{\large H}{|}}{C}}-R \text{ (a secondary alcohol)}$$

GENERAL PROPERTIES OF ALCOHOLS

Physical Properties :-

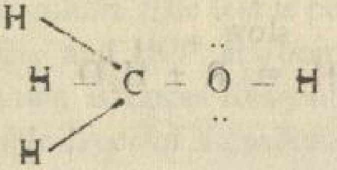
1. The normal alcohols from C_1 to C_{11} are colourless, volatile liquids with a Characteristic smell and a burning taste. Higher members are colourless, odourless, Waxy Solids.

2. The alcohols of lower molecular weights (up to fifth member of the series are soluble in water, the solubility in water decreases with the increase in molecular weights.

3. Boiling Points of alcohols are much higher than those of the alkanes, ethers and ketons of comparable molecular weights. The higher boiling points of alcohols can be attributed to the hydrogen bond formation between the molecules of alcohols.

Chemical Properties :

Characteristic chemical properties of alcohols are mainly due to presence of hydroxy group. The oxygen atom in alcohol is [Sp^3] hybridized forming four equivalent hybrid orbitals. Out of the four [Sp^3] hybridized orbitals two orbitals are completely filled each having a pair of electons. These two pairs of electrons on oxygen are known as unshared or lone pairs of electrons: The remaining two [Sp^3] orbitals are partially filled each having one electron, one of these two partially filled orbitals forms a σ bond with hydrogen while the other forms a σ bond with carbon of the alkyl radical. The bond angle formed is roughly 109°.



The presence of two unshared pairs of electrons on oxygen atom gives basic properties to the hydroxy group in alcohols.

Chemical reactions of alcohols can be divided into three categories :-

(*i*) Chemical reactions in which carbon oxygen bond is broken . In these reactions hydroxy group is replaced by some other group or atom.

(*ii*) Chemical reactions which involve the cleavage of oxygen-hydrogen bond.

(*iii*) Oxidation reactions.

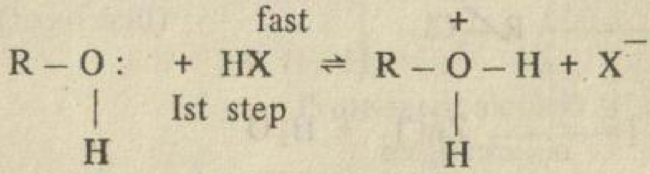
(1) Reactions involving carbon-oxygen cleavage :

Replacement of Hydroxy group by Halogen :- The Hydroxy group of alcohol may be replaced by halogen using several reagents. The most common reagents used for this purpose are (*a*) Hydrogen halides (*HX*), (*b*) Phosphorus trihalides (PX_3), Phosphorus pentahalide (PX_5), (*c*) Thionyl chloride $SOCl_2$.

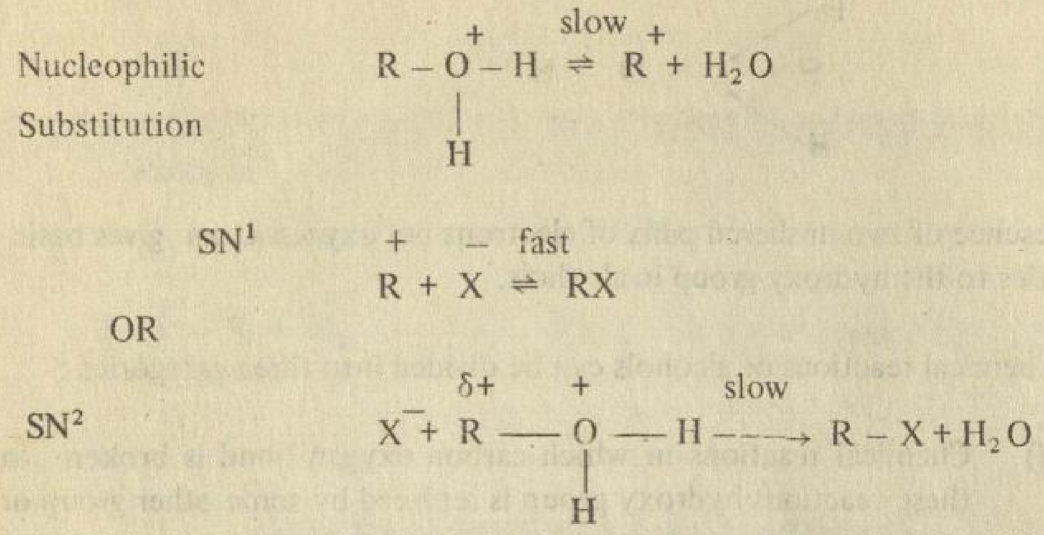
(*a*) **Reaction with acid halides :**

Hydrogen halides, HX, (X = Cl, Br, I) react readily with alcohol forming alkyl halides and water. The reaction is catalysed by acids. These are nucleophilic substitution reactions. The first step is the protonation of alcohol which is the fast step. It is followed by the nucleophilic substitution of the protonated alcohol which may proceed either through SN^1 or SN^2 mechanism depending upon the structure of alcohol.

Protonation :



$$R-\underset{\underset{H}{|}}{O}: + HX \underset{\text{Ist step}}{\overset{\text{fast}}{\rightleftharpoons}} R-\underset{\underset{H}{|}}{\overset{+}{O}}-H + X^-$$



Nucleophilic Substitution

$$R-\underset{\substack{|\\ H}}{\overset{+}{O}}-H \overset{\text{slow}}{\rightleftharpoons} \overset{+}{R} + H_2O$$

SN¹

$$\overset{+}{R} + \overset{-}{X} \overset{\text{fast}}{\rightleftharpoons} RX$$

OR

SN²

$$\overset{-}{X} + \overset{\delta+}{R} — \underset{\substack{|\\ H}}{\overset{+}{O}} — H \xrightarrow{\text{slow}} R-X+H_2O$$

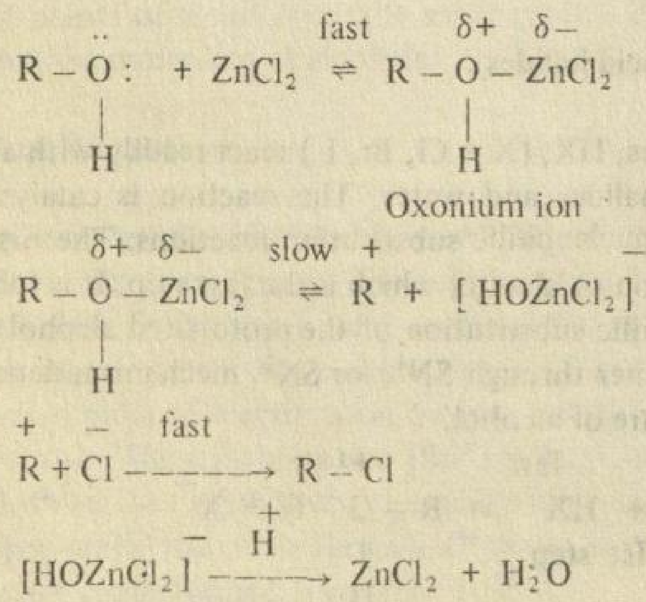
The order of reactivity of alcohols towards a given acid halide is given below

Tertiary alcohol > Secondary alcohol > Primary alcohol

The order of reactivity of hydrogen halides towards a given alcohol is given below :-

HI > HBr > HCl

from the order of reactivities of alcohols and hydrogen halides it is clear that reaction between hydrogen chloride (HCl) and a Primary alcohol (RCH_2OH) would be slow. In fact saturated primary alcohols react with HCl on heating in presence of $ZnCl_2$ as a catalyst. $ZnCl_2$ helps in breaking the carbon-oxygen bond.



$$R-\underset{\substack{|\\ H}}{\ddot{O}}: + ZnCl_2 \overset{\text{fast}}{\rightleftharpoons} R-\underset{\substack{|\\ H}}{\overset{\delta+}{O}}-\overset{\delta-}{ZnCl_2}$$

Oxonium ion

$$R-\underset{\substack{|\\ H}}{\overset{\delta+}{O}}-\overset{\delta-}{ZnCl_2} \overset{\text{slow}}{\rightleftharpoons} \overset{+}{R} + [HOZnCl_2]^{-}$$

$$\overset{+}{R} + \overset{-}{Cl} \xrightarrow{\text{fast}} R-Cl$$

$$[HOZnCl_2]^{-} \xrightarrow{\overset{+}{H}} ZnCl_2 + H_2O$$

Lucas Alcohol Test :- The above reaction is used to distinguish primary, secondary and tertiary alcohols. The test is performed by shaking the alcohol with a mixture of $ZnCl_2$ and HCl at room temperature. The mixture of $ZnCl_2$ and HCl is known as Lucas Reagent. The tertiary alcohols react at once, forming an insoluble layer of haloalkane. The secondary alcohols react comparatively slowly and the product is formed within five minutes. The primary alcohols do not react at room temperature but react on heating to form haloalkane.

(*b*) Reactions with Phosphorus Halides :

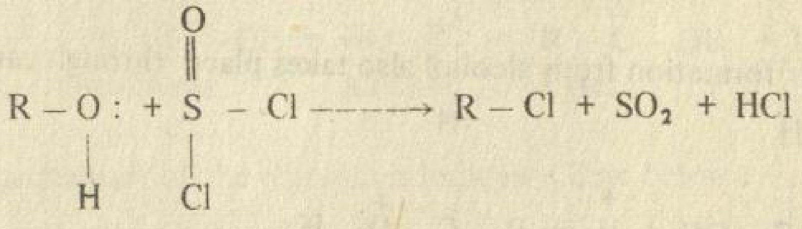
Phosphorus trihalides react with alcohols to form alkylhalides.

$$3\,ROH + PX_3 \longrightarrow 3\,R-X + \underset{\text{orthophosphorus acid}}{H_3PO_3}$$

$$ROH + PX_5 \longrightarrow R-X + HX + POX_3$$

(*c*) Reaction with Thionyl Chloride :

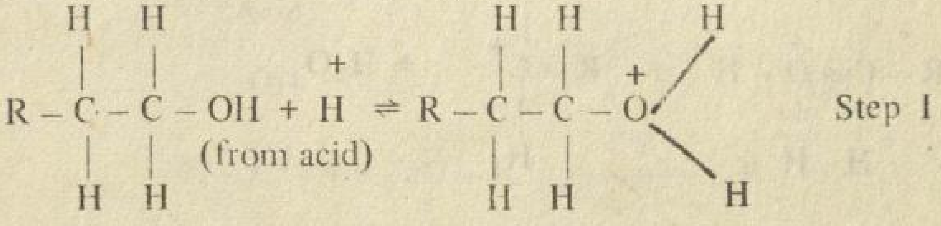
Thionyl chloride is considered as one of the useful reagents by which the hydroxy group may be replaced by a chlorine atom. The products in this method are SO_2 and HCl which could be easily separated from the alkylhalide.



$$R-\underset{\underset{\displaystyle H}{|}}{O}: + \overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle Cl}{|}}{S}} - Cl \longrightarrow R-Cl + SO_2 + HCl$$

2. Dehydration of Alcohols (Elimination reaction):

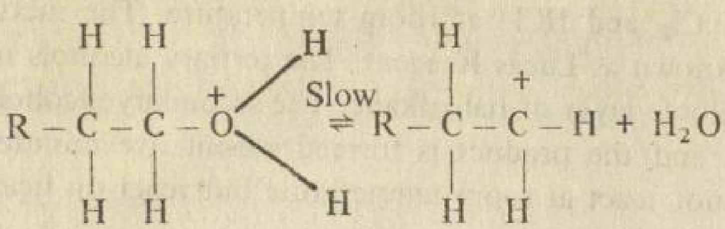
Alcohols can be dehydrated into alkenes in the presence of certain strong acid *e.g.*, sulphuric acid, phosphoric acid.



$$\underset{\text{Alcohol}}{R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-OH} + \underset{\text{(from acid)}}{\overset{+}{H}} \rightleftharpoons \underset{\text{Protonated alcohol or oxonium ion}}{R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\overset{+}{O}\begin{smallmatrix}H\\H\end{smallmatrix}} \qquad \text{Step I}$$

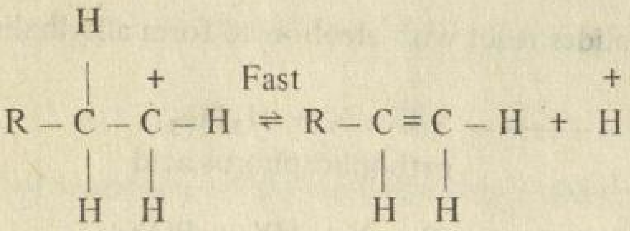
Alcohol

Protonated alcohol or oxonium ion



Step II

Carbonium ion



$$R-\overset{H}{\underset{H}{C}}-\overset{+}{\underset{H}{C}}-H \overset{Fast}{\rightleftharpoons} R-\underset{H}{C}=\underset{H}{C}-H + \overset{+}{H}$$

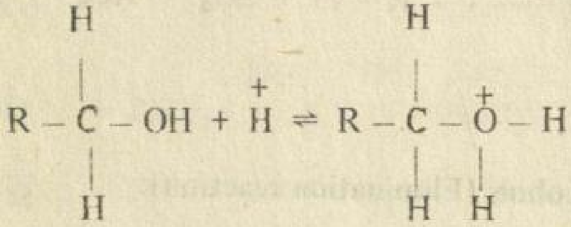
Step III

Alkene

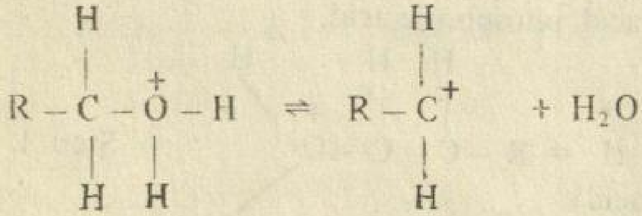
Since in slow or fast determining step only one molecule is involved, therefore, it is a *unimolecular elimination*, E_1, reaction. This elimination reaction takes place at a high temperature. If the temperature is kept low ether, instead of alkenes are formed :

3. Ether Formation :

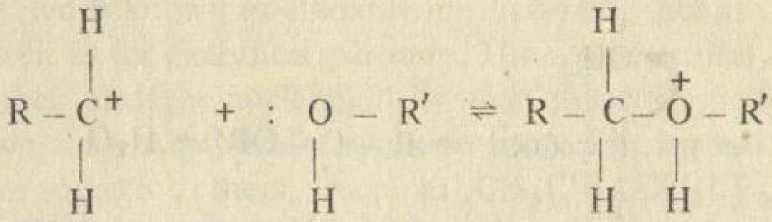
Ether formation from alcohol also takes place through carbonium ion.



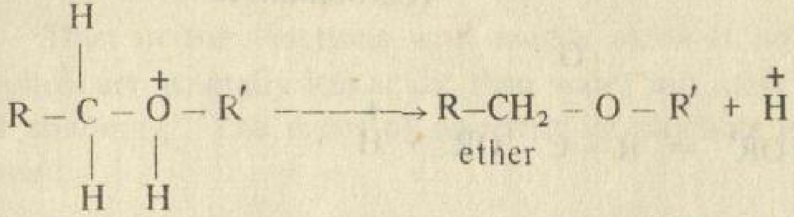
$$R-\overset{H}{\underset{H}{C}}-OH + \overset{+}{H} \rightleftharpoons R-\overset{H}{\underset{H}{C}}-\overset{+}{\underset{H}{O}}-H$$



$$R-\overset{H}{\underset{H}{C}}-\overset{+}{\underset{H}{O}}-H \rightleftharpoons R-\overset{H}{\underset{H}{C^{+}}} + H_2O$$



$$R-\overset{H}{\underset{H}{C^+}} + :\underset{H}{O}-R' \rightleftharpoons R-\overset{H}{\underset{H}{C}}-\overset{+}{\underset{H}{O}}-R'$$

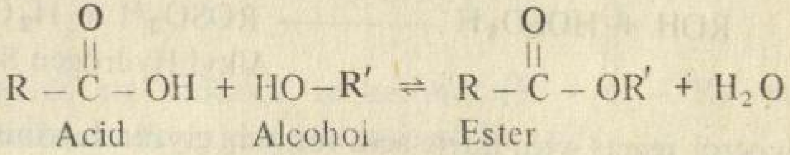


$$R-\overset{H}{\underset{H}{C}}-\overset{+}{\underset{H}{O}}-R' \longrightarrow \underset{\text{ether}}{R-CH_2-O-R'} + \overset{+}{H}$$

(II) Reaction involving oxygen-hydrogen bond:

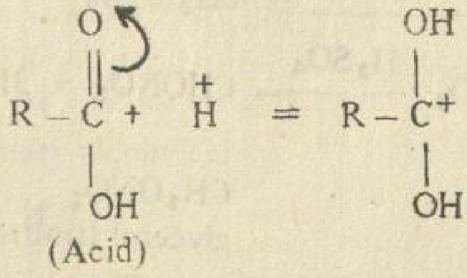
(*i*) *Ester formation :*

When alcohols react with organic acids, esters are obtained. The reaction is catalysed by H^+ ions. Therefore, small amount of sulphuric acid is also added to the reaction mixture. The overall reaction is :

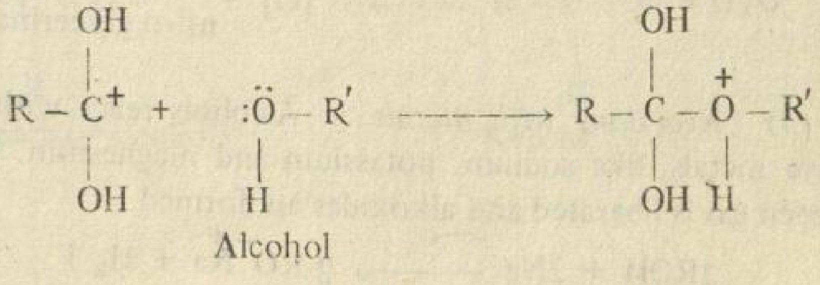


$$\underset{\text{Acid}}{R-\overset{O}{\overset{\|}{C}}-OH} + \underset{\text{Alcohol}}{HO-R'} \rightleftharpoons \underset{\text{Ester}}{R-\overset{O}{\overset{\|}{C}}-OR'} + H_2O$$

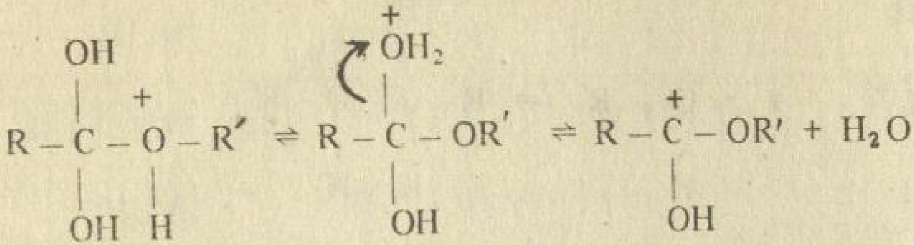
The mechanism of the reaction is indicated here below :



$$\underset{\text{(Acid)}}{R-\overset{O}{\overset{\|}{\underset{OH}{C}}}} + \overset{+}{H} = R-\overset{OH}{\underset{OH}{C^+}}$$

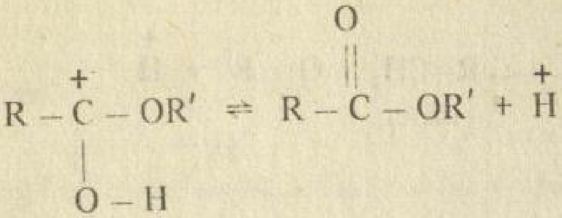


$$R-\overset{OH}{\underset{OH}{C^+}} + :\underset{\underset{\text{Alcohol}}{H}}{\ddot{O}}-R' \longrightarrow R-\overset{OH}{\underset{OH}{C}}-\overset{+}{\underset{H}{O}}-R'$$



$$R-\underset{OH}{\overset{OH}{C}}-\underset{H}{\overset{+}{O}}-R' \rightleftharpoons R-\underset{OH}{\overset{\overset{+}{O}H_2}{C}}-OR' \rightleftharpoons R-\underset{OH}{\overset{+}{C}}-OR' + H_2O$$

(Carbonium ion)



$$R-\underset{O-H}{\overset{+}{C}}-OR' \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-OR' + \overset{+}{H}$$

Alkyl halides are considered as esters of hydrogen halides with alcohols. Nitric acid and sulphuric acid react with alcohols to form alkyl nitrate and alkyl hydrogen sulphate respectively.

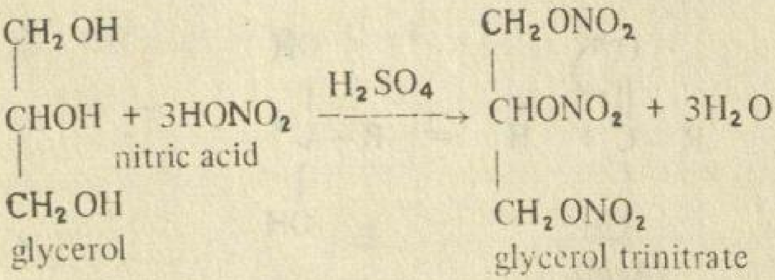
$$ROH + HONO_2 \xrightarrow{H_2SO_4} RONO_2 + H_2O$$

(Nitric Acid) Alkyl nitrate

$$ROH + HOSO_3H \xrightarrow{90^\circ C} ROSO_3H + H_2O$$

Alkyl Hydrogen Sulphate

Glycerol reacts with nitric acid forming glycerol trinitrate which is also known as nitroglycerine. This ester is used as an explosive.



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3HONO_2 \xrightarrow{H_2SO_4} \begin{array}{l} CH_2ONO_2 \\ | \\ CHONO_2 \\ | \\ CH_2ONO_2 \end{array} + 3H_2O$$

glycerol — nitric acid — glycerol trinitrate or nitro glycerine

(*ii*) *Reactions with metals* :- Alcohols react with strongly electropositive metals, like sodium, potassium and magnesium. In these reactions hydrogen gas is liberated and alkoxides are formed.

$$2ROH + 2Na \longrightarrow 2\,R\overset{-}{O}\,\overset{+}{Na} + H_2\uparrow$$

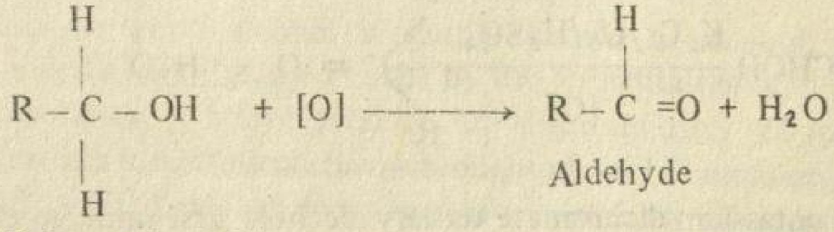
RO^- ion is known as alkoxide ion. Alkoxide ions are important for synthetic as well as for analytical purposes. The synthetic uses of alkoxide ions are due to their stronger nucleophilicity than the corresponding alcohols and hydroxide ions. Analytically alkoxide formation is used to distinguish alcohols from organic ethers, such as $CH_3CH_2OCH_2CH_3$ (diethyl ether) and CH_3OCH_3(dimethyl ether)Ethers do not react with metals.

Thus in the reactions with metals alcohols behave like weak acids. Alcohols are generally less acidic than water but more acidic than acetylenes and ammonia . The order of reactivity of alcohols towards metal is given below :

CH_3OH > Primary alcohols > Secondary alcohols > Tertiary alcohols

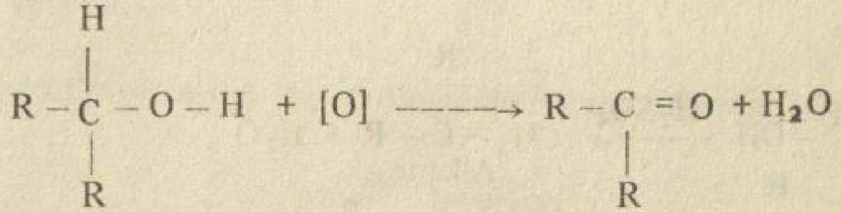
(III) Oxidations of Alcohols :

Oxidation of alcohols involves the breaking of carbon-hydrogen and oxygen hydrogen bonds. Thus a molecule of hydrogen is eliminated forming a double bond between carbon and oxygen. Primary alcohols are oxidised to aldehydes ($R-\overset{\overset{O}{\parallel}}{C}-H$) which can further be oxidised to carboxylic acids. Secondary alcohols are oxidised to ketones ($R-\overset{\overset{O}{\parallel}}{C}-R$) which under vigorous conditions can be oxidised to carboxylic acids.



$$R-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-OH + [O] \longrightarrow R-\overset{\overset{H}{|}}{C}=O + H_2O$$

(Primary alcohols) Aldehyde

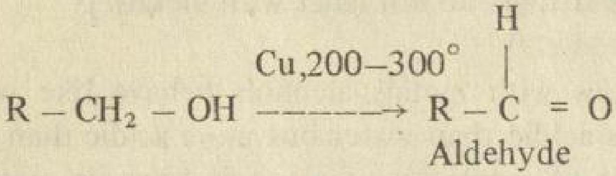


$$R-\underset{\overset{|}{R}}{\overset{\overset{H}{|}}{C}}-O-H + [O] \longrightarrow R-\underset{\overset{|}{R}}{C}=O + H_2O$$

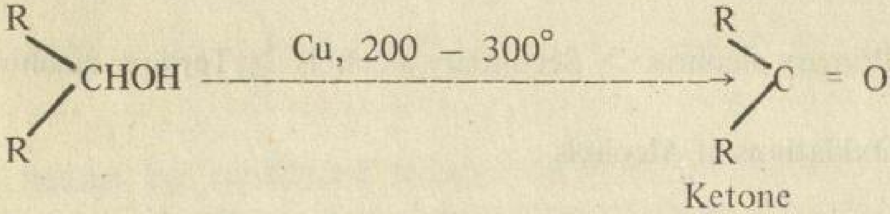
(Secondary alcohol) Ketone

In tertiary alcohols there is no hydrogen at carbon bearing hydroxy group, therefore, they are most difficult to be oxidised. Primary and secondary alcohols can be oxidised by the following two methods :

(*a*) By passing the vapours of alcohols through a tube packed with copper turnings heated to 200 – 300°C.



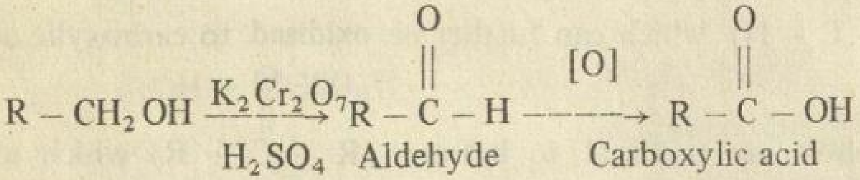
$$R-CH_2-OH \xrightarrow{Cu,200-300^\circ} \underset{\text{Aldehyde}}{R-\overset{\overset{H}{|}}{C}=O}$$



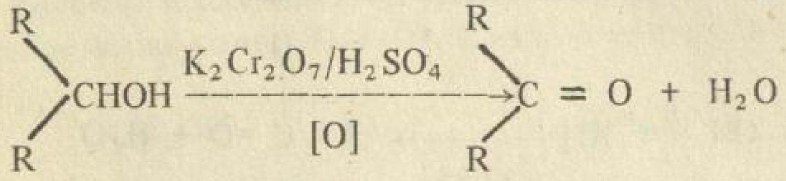
R
R
CHOH
Cu, 200 – 300°
R
R
C = O
Ketone

This process is known as *dehydrogenation.*

(*b*) Primary or secondary alcohols can also be oxidised with chromic acid (H_2CrO_4) or with a mixture of potassium dichromate and sulphuric acid.

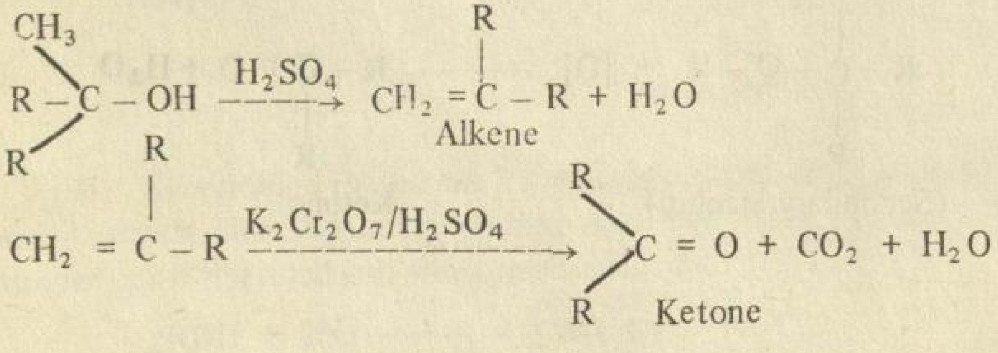


$$R-CH_2OH \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Aldehyde}}{R-\overset{\overset{O}{\|}}{C}-H} \xrightarrow{[O]} \underset{\text{Carboxylic acid}}{R-\overset{\overset{O}{\|}}{C}-OH}$$



R
R
CHOH
$K_2Cr_2O_7/H_2SO_4$
[O]
R
R
C = O + H_2O

With acidic potassium dichromate tertiary alcohols first undergo elimination reaction to give alkenes which are subsequently oxidised to carbonyl compounds.



CH_3
R – C – OH
R
H_2SO_4
R
CH_2 = C – R + H_2O
Alkene
R
CH_2 = C – R
$K_2Cr_2O_7/H_2SO_4$
R
R
C = O + CO_2 + H_2O
Ketone

Methanol (CH_3OH)

Methanol or methyl alcohol is also known as wood spirit. The name wood spirit indicates the source of its production by the destructive distillation of wood. Wood is heated above 160°C in the absence of air. Various products are obtained in the form of gas, liquid and tarry matter, while charcoal is left in the retort. The liquid portion consists mainly of methanol, acetone and acetic acid. Methanol may be obtained from this mixture.

Cheaper and pure methanol is obtained from water-gas ($CO + H_2$) by the application of *Fischer Tropsch Process.* Certain metal oxides like ZnO, Cr_2O_3 are used as Catalysts.

$$CO + 2H_2 \xrightarrow[400^{\circ}C,\ \text{high pressure.}]{\text{Metal oxides}} CH_3OH$$

Methanol is a colourless liquid having characteristic odour. It is highly toxic, and even small amounts when taken internally have been known to cause blindness or even death. Methanol is an excellent solvent and is used in the manufacture of paints and varnishes. It is also used as an antifreez and to denature ethanol in order to make it unfit for drinking purposes.

Ethanol (C_2H_5OH)

Ethanol or ethyl alcohol is simply known as alcohol. Now-a-days ethanol is mostly manufactured either by the fermentation of carbohydrates (generally molasses – a bye products of sugar industry) or from ethane. Fermentation is a biochemical change brought about by micro-organisms e.g., bacteria and yeast. Yeast produces certain complex nitrogenous compounds known as enzymes. These enzymes act as catalysts in changing the carbohydrates into ethanol.

In case of molasses as the starting material the following reactions take place.

$$\underset{\text{Sucrose in molasses}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{Enzyme (Present in Yeast)}]{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[\text{Enzyme (Present in Yeast)}]{\text{Zymase}} \underset{\text{Ethanol}}{2C_2H_5OH} + 2CO_2$$

The fermentation of starch also gives ethyl alcohol.

Alcohol obtained by the fermentation process is generally about 13% because micro-organisms cannot function as catalyst beyond this concentration. It is further purified and concentrated by fractional distillation. By this method ethyl alcohol of about 95.6% concentration is obtained. It is known as rectified spirit. If 100% ethanol (absolute alcohol) is required, CaO (quick lime) is added to the rectified spirit which absorbs water and gives absolute ethanol on distillation. Alcohol to be used for purposes other than drinking is denatured by adding some amount of methanol and other chemicals like formaldehyde, phenol, pyridine or benzene to make it unifit for drinking. The denatured alcohol is also known as *methylated spirit.* Drinking of methylated spirit is very dangerous.

Ethers :

The name "Ether" is applied to organic compounds that, contain an oxygen bonded to two alkyl groups ($R-O-R$). They may be regarded as the derivatives of alcohols where the hydroxyl hydrogen of the alcohol has been substituted by an alkyl group.

$$R-O-H \longrightarrow R-O-R$$

They may be represented by a general formula $(R)_2O$ or $R-O-R$. When the two alkyl groups in an ether are identical it is known as symmetrical or simple ether such as diethyl ether $CH_3-CH_2-O-CH_2-CH_3$

The ether is known as unsymmetrical or mixed ether, when the two groups are different such as,

$$\underset{\text{methyl ethyl ether}}{CH_3-O-CH_2-CH_3}$$

Nomenclature :

Common System : Ethers are usually, called by their common names. For naming the individual members the names of the alkyl groups are placed before the word ether.

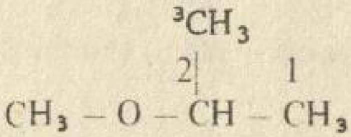
CH_3-O-CH_3 dimethyl ether

$CH_3-O-CH_2-CH_3$ methyl ethyl ether

IUPAC System : According to the IUPAC system, an ether is considered as the derivative of an alkane in which a hydrogen is replaced by an alkoxy group (R O –). The position number and name of alkoxy group is placed before the name of corresponding alkane.

$CH_3-O-CH_2-CH_3$ methoxy ethane

$CH_3-CH_2-O-CH_2-CH_3$ ethoxy ethane

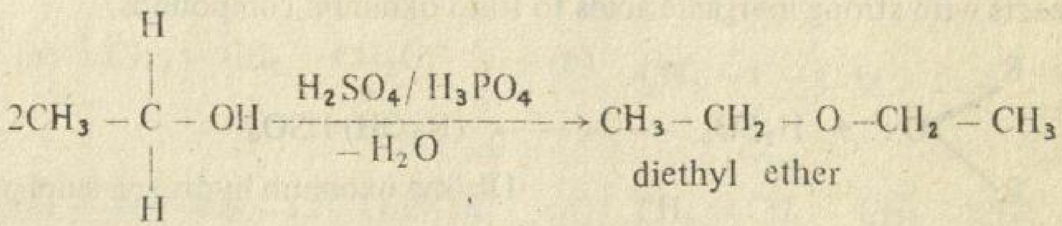


$$CH_3-O-\underset{2}{\overset{^3CH_3}{\overset{|}{C}H}}-\overset{1}{C}H_3$$

2-methoxy propane

General Methods of Preparation :-

1. *From Alcohols :* By heating an excess of alcohol with concentrated sulphuric acid or phosphoric acid.



$$2CH_3-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-OH\xrightarrow[-H_2O]{H_2SO_4/H_3PO_4}CH_3-CH_2-O-CH_2-CH_3$$

diethyl ether

ethyl alcohol

This method is used for preparing ethers on commercial scale.

2. *From Halo-alkanes (Williamson Ether Synthesis).*

Ether can be obtained by heating sodium or potassium alkoxide with an alkyl halide.

Alkoxide ion (RO⁻) can be obtained by treating metallic sodium or potassium with an alcohol.

$$2\,ROH + 2\,Na \longrightarrow 2RO\overset{-}{}\overset{+}{Na} + H_2\uparrow$$

$$R\bar{O} + R \text{-----} X \xrightarrow{SN} R - O - R + X^-$$

As mentioned earlier it is a nucleophilic substitution reaction.

General Properties :

Physical Properties :

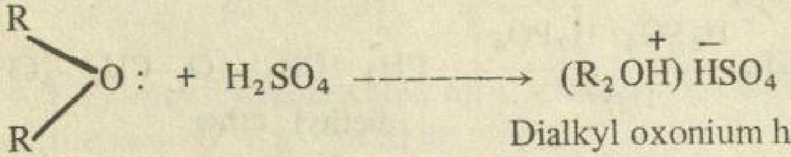
Ethers are pleasant smelling substances. They have generally low boiling points. Their boiling points are comparable to those of alkanes of the same molecular weights. They are lighter than water. They have very low solubility in water.

Chemical Properties :

Ethers are quite unreactive, Ether linkage (R – O – R) is sufficiently stable towards bases, oxidising agents and reducing agents.

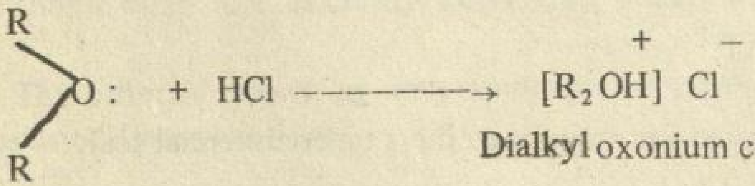
1. *Formation of Stable Salts :*

Ether has unshared pair of electrons and so it can act as a weak base. It reacts with strong inorganic acids to form oxonium compounds.



$$R_2O: + H_2SO_4 \longrightarrow (R_2\overset{+}{O}H)\overset{-}{HSO_4}$$

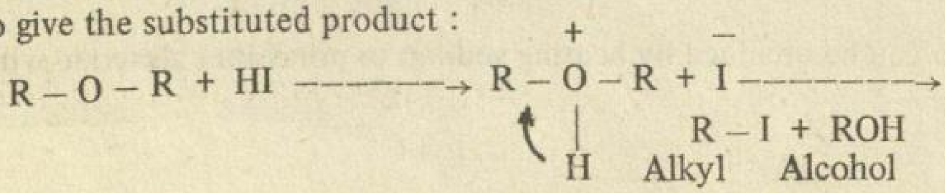
Dialkyl oxonium hydrogen sulphate



$$R_2O: + HCl \longrightarrow [R_2\overset{+}{O}H]\ \overset{-}{Cl}$$

Dialkyl oxonium chloride.

If the anion of the acid is a strong nucleophile it attacks on oxonium ion to give the substituted product :



$$R-O-R + HI \longrightarrow R-\underset{\displaystyle H}{\overset{+}{O}}-R + \overset{-}{I} \longrightarrow \underset{\text{Alkyl iodide}}{R-I} + \underset{\text{Alcohol}}{ROH}$$

2. *Formation of Alcohols :*

Ethers on heating with sulphuric acid under pressure, form the corresponding alcohols

$$R_2O + H_2O \xrightarrow{H_2SO_4} 2\,ROH$$

Use of Diethyl Ether :

Diethyl ether ($C_2H_5 - O - C_2H_5$) commonly known as ether is the most important member of this homologous series. Ether is used as an organic solvent in laboratories as well as in industries. It is also used as a general anaesthetic. Ether is highly inflammable and very volatile (b.p.34.6°C).

QUESTIONS

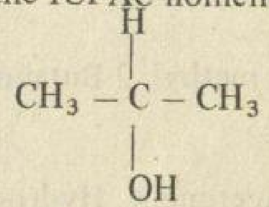
1. Write the structures of the following compounds :

(*a*) 3 – Hexanol (*b*) 1 – Propanol
(*c*) 1, 3– Butandiol (*d*) 2 – Methyl 1, 3 Pentandiol
(*e*) 2, 2 dimethyl –1– Propanol (*f*) Ethyl isopropyl ether
(*g*) Di-n-propyl ether

2. Name the following according to the IUPAC nomenclautre:

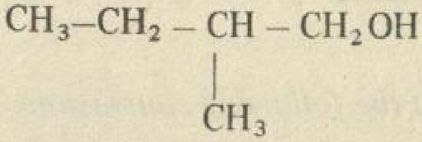
(*a*) $CH_3 - CH_2 - CH_2OH$

(*b*)



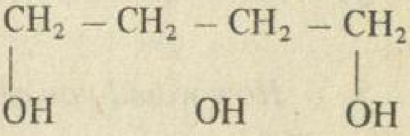
$CH_3 - \overset{H}{\underset{OH}{C}} - CH_3$

(*c*)



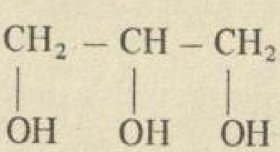
$CH_3-CH_2 - \underset{CH_3}{CH} - CH_2OH$

(d)



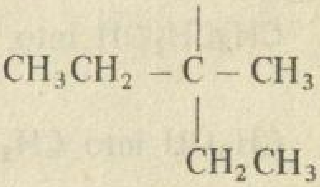
$\underset{OH}{CH_2} - CH_2 - CH_2 - \underset{OH}{CH_2}$

(*e*)

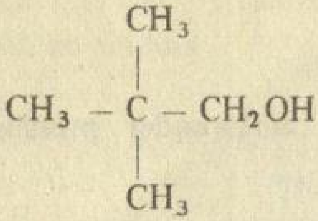


$\underset{OH}{CH_2} - \underset{OH}{CH} - \underset{OH}{CH_2}$

(*f*)



$CH_3CH_2 - \overset{OH}{\underset{CH_2CH_3}{C}} - CH_3$

(g) 

$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2OH$$

(h) $CH_3-O-CH_2-CH_2-CH_2-CH_3$

(i) $CH_3-CH_2-O-CH_2-CH_3$

3. Construct five isomeric alcohols from the molecular formula $C_5H_{12}O$ and suggest IUPAC names.

4. *Write complete chemical equations for the following reactions:*

(a) Ethanol + Hydrobromic acid $\longrightarrow$

(b) Propanol + Phosphorus tribromide $\longrightarrow$

(c) Methanol + Phosphorus pentachloride $\longrightarrow$

(d) Ethanol + Thionyl chloride $\longrightarrow$

(e) Glycerol + Sulphuric acid $\longrightarrow$

(f) Ethanol + Sulphuric acid $\longrightarrow$

(g) 1 - Butanol $\xrightarrow[300^\circ C]{Cu}$

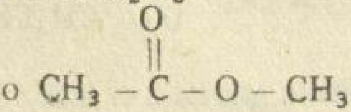
(h) 1 - Butanol $\xrightarrow{K_2Cr_2O_7 + H_2SO_4}$

(i) 2 methyl 2 Butanol $\xrightarrow[300^\circ C]{Cu}$

(j) Acetone + Hydrogen $\xrightarrow{\text{catalyst}}$

5. *How would you accomplish the following conversions ?*

(a) CH_3CH_2OH into C_2H_6

(b) CH_3OH into 

$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-O-CH_3$$

(c) CH_3CH_2OH into CH_3CHO

(*d*) CH_3CH_2OH into $CH_3-CH_2OCH_2CH_3$

(*e*) $C_{12}H_{22}O_{11}$ into C_2H_5OH

6. *Show how you could distinguish by simple chemical tests between :*

(*a*) 1 - Butanol and 2 - Butanol

(*b*) Ethanol and 2 methyl - 2 Propanol

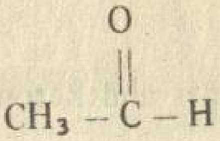
(*c*) 2 - Butanol and 2-methyl-2-Propanol

(*d*) CH_3OH and CH_3Cl

(*e*) CH_3OCH_3 and CH_3CH_2OH

7. What Product would you get upon :

(*a*) Oxidation and (*b*) Reduction of



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

8. Define the following terms. Give suitable examples :

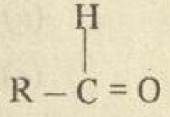
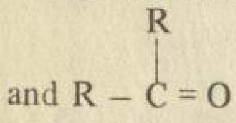
(*a*) Dehydrogenation (*b*) Dehydration

(*c*) Carbonium ion (*d*) Oxonium ion

(*e*) β - Elimination

CHAPTER 17

ALDEHYDES AND KETONES

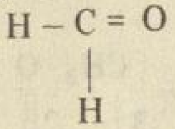
Aldehydes and ketones are characterized by the presence of carbonyl group. $>C=O$, and are collectively called carbonyl compounds. In an aldehyde, carbon of carbonyl group is attached to one hydrogen and one carbon or with two hydrogens while in a ketone, carbonyl carbon is attached to two carbons. The general formulae for aldehydes and ketones are  $R-\overset{\overset{H}{|}}{C}=O$ and  $R-\overset{\overset{R}{|}}{C}=O$ respectively. Aldehydic group is represented as $-CHO$, while ketonic group is represented as $>C=O$.

NOMENCLATURE

Aldehydes :

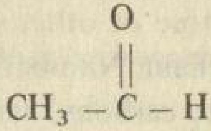
(*a*) *Common System* : The common names of aldehydes are derived from the common names of the corresponding carboxylic acids which the aldehydes produce on oxidation. The ending - ic of the name of carboxylic acid is replaced with the ending - aldehyde. The position of substituents on the chain is indicated by the Greek $\alpha, \beta, \gamma, \delta$, etc. The carbon atom, adjacent to the carbonyl group is considered as α carbon and the next one as β and so on.

Examples :



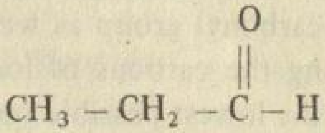
$$H-\underset{\displaystyle H}{\underset{|}{C}}=O$$

Formaldehyde



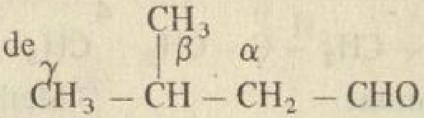
$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-H$$

Acetaldehyde



$$CH_3-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-H$$

propionaldehyde

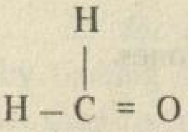


$$\overset{\gamma}{C}H_3-\overset{\displaystyle CH_3}{\overset{|\,\beta}{C}H}-\overset{\alpha}{CH_2}-CHO$$

β Methyl - butyraldehyde

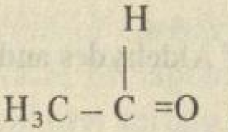
(*b*) *IUPAC System* : The longest continuous carbon chain containing aldehyde group is chosen. From the name of the corresponding alkane containing the same number of carbons as the longest chain, the ending – e is replaced by the ending – al. To indicate the positions of substituents numbering starts from carbonyl carbon.

Examples :



$$H-\overset{\displaystyle H}{\overset{|}{C}}=O$$

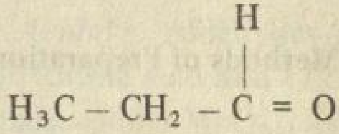
Methanal



$$H_3C-\overset{\displaystyle H}{\overset{|}{C}}=O$$

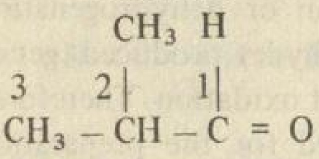
Ethanal

;



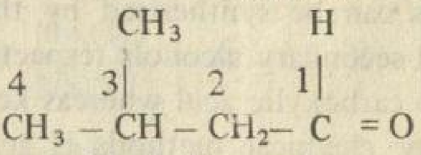
$$H_3C-CH_2-\overset{\displaystyle H}{\overset{|}{C}}=O$$

Propanal



$$\overset{3}{CH_3}-\overset{\displaystyle CH_3}{\overset{2|}{CH}}-\overset{\displaystyle H}{\overset{1|}{C}}=O$$

2-Methyl propanal



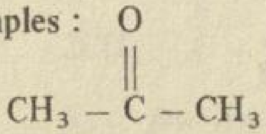
$$\overset{4}{CH_3}-\overset{\displaystyle CH_3}{\overset{3|}{CH}}-\overset{2}{CH_2}-\overset{\displaystyle H}{\overset{1|}{C}}=O$$

3 - Methyl butanal

KETONES

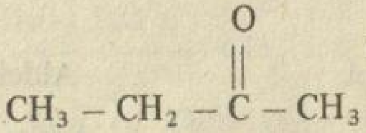
(*a*) *Common System* : The common names of the ketones are obtained by naming the alkyl groups attached to carbonyl group, followed by the separate word ketone.

Examples :



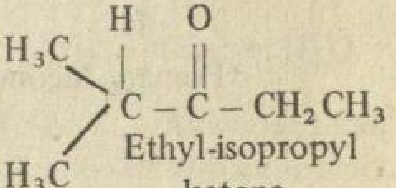
$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$$

Dimethyl ketone
(Acetone)



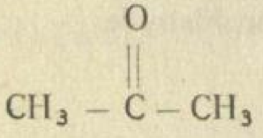
$$CH_3-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$$

Ethyl-methyl ketone



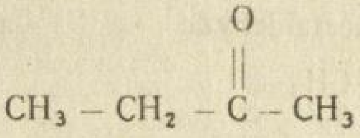
Ethyl-isopropyl ketone

(*b*) *IUPAC System* : In this system the name of ketone is derived from the name of the alkane containing the same number of carbons as the longest continuous carbon chain having carbonyl group of ketone. The ending of the name of corresponding alkane is replaced with the ending 'one'. Position of carbonyl group as well as those of other substituents is indicated by numbering the carbons of longest chain. Numbering starts from the end which gives the lowest possible number to carbonyl carbon.



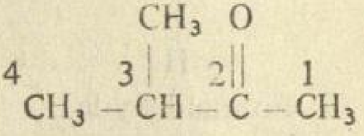
$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

Propanone



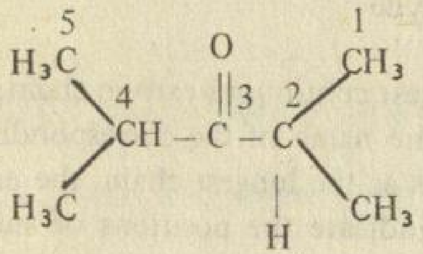
$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

Butanone



$\overset{4}{CH_3}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{3}{CH}}-\overset{\overset{\displaystyle O}{\|}}{\underset{2}{C}}-\overset{1}{CH_3}$

3-Methyl-2-Butanone

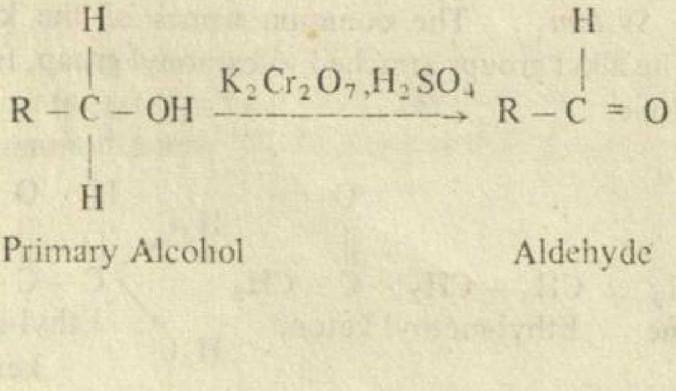


2,4-Dimethyl-3-Pentanone

General Methods of Preparation of Aldehydes and Ketones :

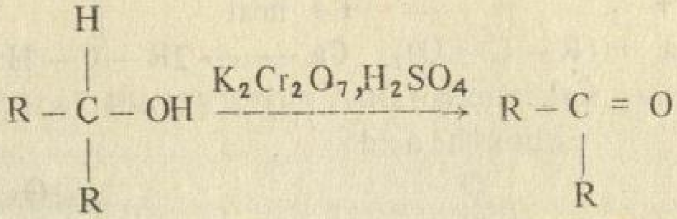
1. *By the Oxidation or dehydrogenation of Alcohols* : Aldehydes and ketones can be synthesised by the oxidation or dehydrogenation of primary and secondary alcohols respectively. Aldehydes produced get easily oxidized to carboxylic acid whereas ketones resist oxidation. Therefore, the oxidation by chemical methods is generally used for the preparation of ketones. Aldehydes are conveniently prepared by the catalytic dehydrogenation of primary alcohols in vapour state.

(*a*) *Oxidation of Alcohols* :



$$R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH \xrightarrow{K_2Cr_2O_7,H_2SO_4} R-\overset{\overset{\displaystyle H}{|}}{C}=O$$

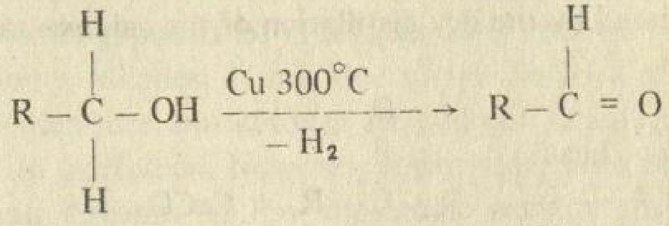
Primary Alcohol　　　　　　　　Aldehyde



$$R-\overset{\overset{H}{|}}{\underset{\underset{R}{|}}{C}}-OH \xrightarrow{K_2Cr_2O_7, H_2SO_4} R-\underset{\underset{R}{|}}{C}=O$$

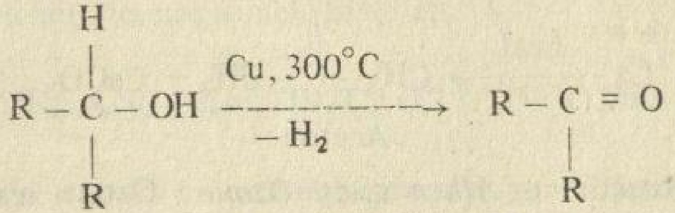
Secondary Alcohol Ketone

(*b*) *Catalytic dehydrogenation of Alcohols :*



$$R-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-OH \xrightarrow[-H_2]{Cu\ 300^\circ C} R-\overset{\overset{H}{|}}{C}=O$$

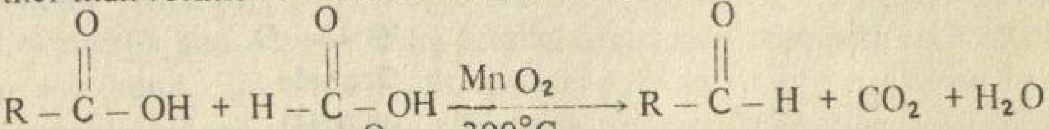
Primary Alcohol Aldehyde



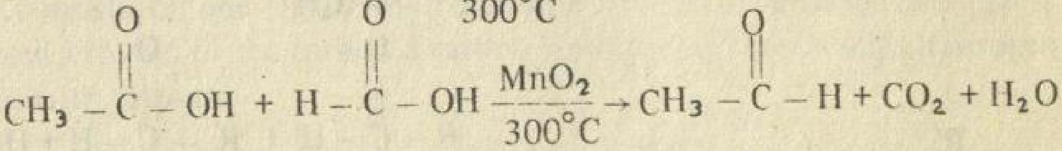
$$R-\overset{\overset{H}{|}}{\underset{\underset{R}{|}}{C}}-OH \xrightarrow[-H_2]{Cu, 300^\circ C} R-\underset{\underset{R}{|}}{C}=O$$

Secondary Alcohol Ketone

2. *By the Pyrolysis of Carboxylic Acids* : Aldehydes may be prepared by passing a mixture of vapours of formic acid and of a carboxylic acid other than formic acid over certain metallic oxides MnO_2.

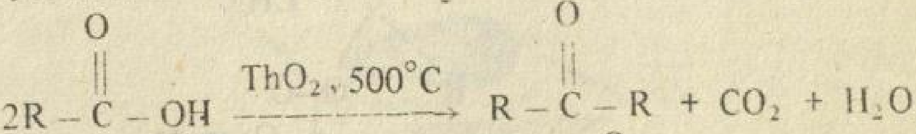


$$R-\overset{\overset{O}{\|}}{C}-OH + H-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[300^\circ C]{MnO_2} R-\overset{\overset{O}{\|}}{C}-H + CO_2 + H_2O$$

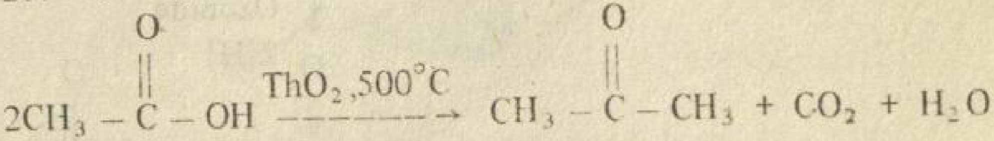


$$CH_3-\overset{\overset{O}{\|}}{C}-OH + H-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[300^\circ C]{MnO_2} CH_3-\overset{\overset{O}{\|}}{C}-H + CO_2 + H_2O$$

Ketones may also be prepared in the same way by passing the vapours of a carboxylic acid over a catalyst ThO_2 at 500°C.



$$2R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{ThO_2, 500^\circ C} R-\overset{\overset{O}{\|}}{C}-R + CO_2 + H_2O$$



$$2CH_3-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{ThO_2, 500^\circ C} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + CO_2 + H_2O$$

3. *By heating Salts of Carboxylic Acids:* Aldehydes can be obtained by the dry distillation of mixture of calcium salt of formic acid and calcium salt of any carboxylic acid.

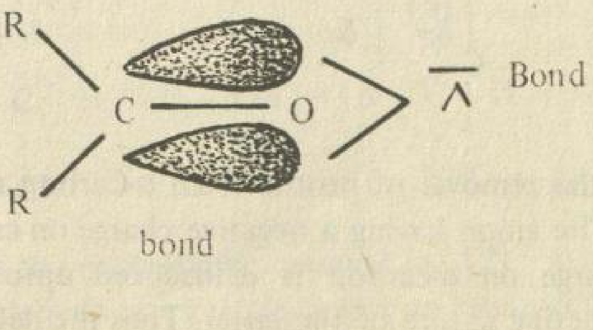
GENERAL PROPERTIES OF ALDEHYDES AND KETONES

Physical Properties :

The first member of the aldehyde family (formaldehyde $H - \overset{\overset{O}{||}}{C} - H$) is in the gaseous state while most of the aldehydes and ketones are colourless liquids. The boiling points of aldehydes and ketones are higher than those of corresponding Alkanes. This is due to the Polarity of the carbonyl group. Most of the aldehydes and ketones are pleasant smelling compounds and are usually used in perfumes. However, lower aldehydes have unpleasant smell. Aldehydes and ketones of low molecular weights are miscible with water while compounds containing five carbon atoms or more are insoluble. All aldehydes and ketones are soluble in ether.

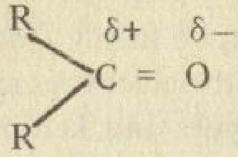
STRUCTURE AND REACTIVITY OF ALDEHYDES AND KETONES

The carbon atom of carbonyl group in an aldehyde or ketone is [Sp^2] hybridized giving three equivalent coplanar orbitals with an angle of 120° between any two of them. The remaining one P orbital is perpendicular to the plane of hybridized orbitals. Similarly the oxygen atom of the carbonyl group is also [Sp^2] hybridized. One [Sp^2] hydridized orbital of carbon formsσ bond with a [Sp^2] hybridized orbital of oxygen. The unhybridized p orbitals of carbon and oxygen being parallel overlap sidewise with each other to form a π bond. Thus the resulting double bond between carbon and oxygen consists of one sigma bond and one π bond. The other two [Sp^2] hybridized orbitals of the carbonyl carbon form two σ bonds with hydrogen atoms or with carbons.

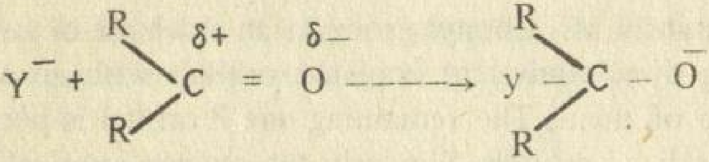


(Fig. 17.1)

Oxygen being more electronegative than carbon attracts the mobile π electrons towards itself. Hence there is a partial positive charge on the carbon of the carbonyl group and a partial negative charge on the oxygen. Thus the carbonyl group is a polar group and its carbon is electrophilic while oxygen is nucleophilic.

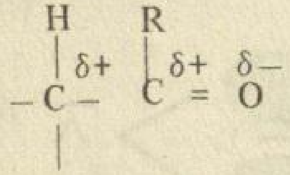


Due to the presence of carbon-oxygen double bond, aldehydes and ketones also undergo addition reactions like alkenes. Aldehydes and ketones molecules are flat near the carbonyl group. Hence, partially positively charged carbon of the carbonyl group is susceptible to an easy attack by a nucleophile. Therefore characteristic reactions of aldehydes and ketones are nucleophilic addition as compared to electrophilic addition reactions of unsaturated hydrocarbons.



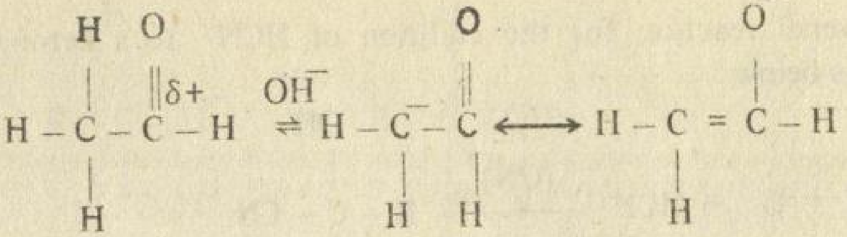
The properties of aldehydes and ketones in which the carbonyl group is involved are similar. However, some of the reactions of aldehydes are different from those of ketones, because the aldehydes have a hydrogen atom bonded to the carbonyl group.

The other important effect of the polarity of carbonyl group is that it induces a small positive charge on the adjacent carbon (α - C). This inductive effect will make the bond between carbon and hydrogen slightly polar rendering hydrogen some acidic character.



$$\underset{|}{\overset{\overset{H}{|}\,\delta+}{-C-}}\;\overset{\overset{R}{|}\,\delta+}{C}=\overset{\delta-}{O}$$

After the removal of proton from α-Carbon there is a negative charge on carbon. The anion having a negative charge on carbon is called *carbanion.* Negative charge on α-carbon is delocalized upto carbonyl group due to electron attracting nature of the latter. Thus the delocalization of this charge stabilises the carbanion. The stability of carbanion is also an important factor of the acidic nature of α-hydrogens.



$$H-\underset{H}{\overset{H}{C}}-\overset{\overset{O}{\parallel}\,\delta+}{C}-H \overset{OH^-}{\rightleftharpoons} H-\underset{H}{\bar{C}}-\underset{H}{\overset{\overset{O}{\parallel}}{C}} \longleftrightarrow H-\underset{H}{C}=\overset{O^-}{C}-H$$

Chemical Properties :

The chemical properties of aldehydes and ketones can be divided into following types :-

(*a*) Nucleophilic addition reactions.

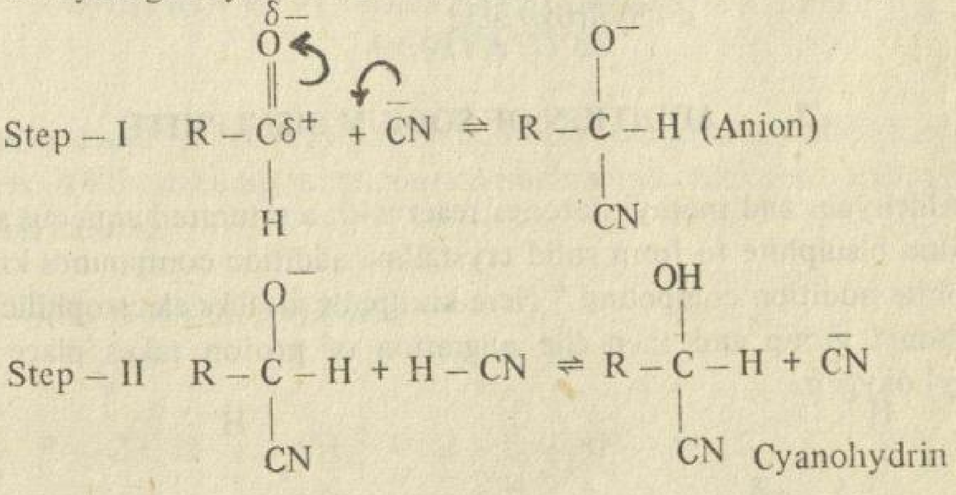
(*b*) Reactions due to α-hydrogens.

(c) Oxidation and Reduction reactions.

(a) **Nucleophilic Addition Reactions :**

1. ADDITION OF HYDROGEN CYANIDE TO ALDEHYDES AND KETONES

Hydrogen cyanide adds to carbon-oxygen double bond of aldehydes and ketones to produce cyanohydrins. The reaction is carried out by adding acetic acid or mineral acid into the mixture of aldehyde or ketone and sodium or potassium cyanide. Action of acid on sodium or potassium cyanide produces hydrogen cyanide . The addition takes place in two steps.

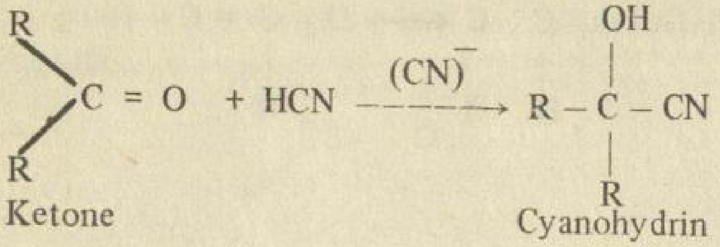


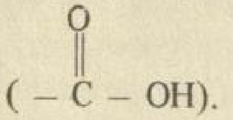
$$\text{Step – I}\quad R-\underset{H}{\overset{\overset{\delta-}{O}}{\overset{\parallel}{C}}}\delta^+ + \bar{C}N \rightleftharpoons R-\underset{CN}{\overset{O^-}{C}}-H\ \text{(Anion)}$$

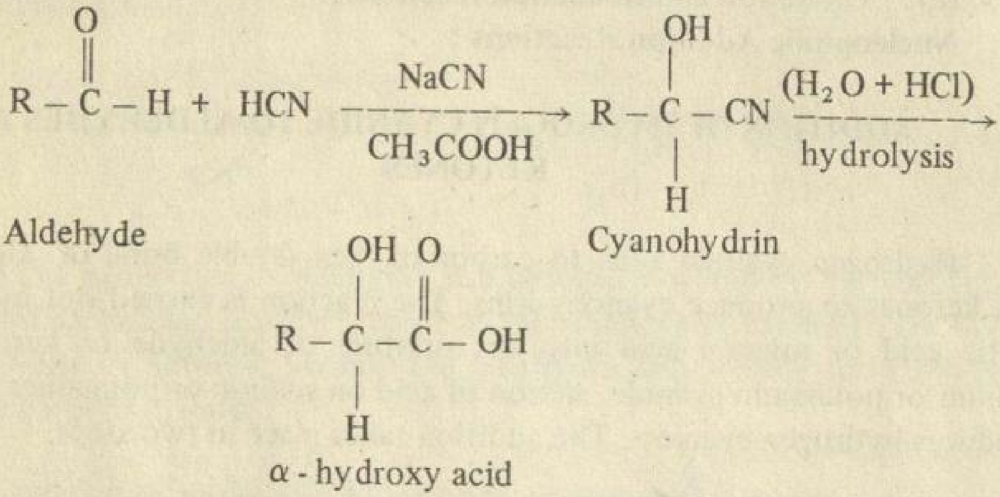
$$\text{Step – II}\quad R-\underset{CN}{\overset{O^-}{C}}-H + H-CN \rightleftharpoons R-\underset{CN}{\overset{OH}{C}}-H + \bar{C}N\quad \text{Cyanohydrin}$$

In the first step the nucleophilic cyanide ion CN^- attacks the electrophilic carbon of an aldehyde or a ketone to give an intermediate anion. In the second step the anion reacts with HCN taking proton from it. The cyanide ion which reacts with an aldehyde or a ketone in step I is regenerated in Step II. Therefore the cyanide ion acts as a catalyst and its presence in small amounts is essential for the reaction.

The overall reaction for the addition of HCN to a ketone can be represented as below :



The cyanohydrins are very important from synthetic point of view. Cyanide group is readily hydrolysed in the presence of acid or alkali to form carboxylic group  $(-\overset{O}{\overset{\|}{C}}-OH)$. Thus the hydrolysis of cyanohydrins produces α-hydroxy carboxylic acid.



$$R-\overset{O}{\overset{\|}{C}}-H + HCN \xrightarrow[CH_3COOH]{NaCN} R-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CN \xrightarrow[hydrolysis]{(H_2O + HCl)} R-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-OH$$

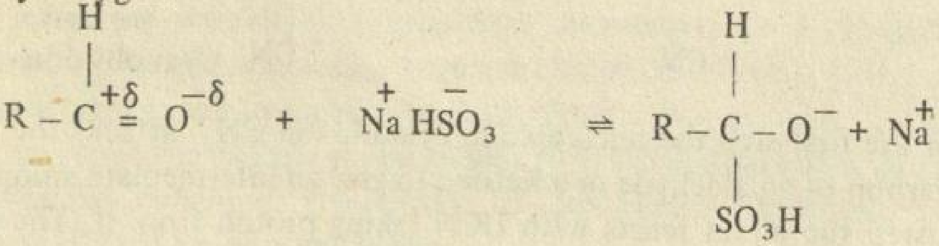
Aldehyde

Cyanohydrin

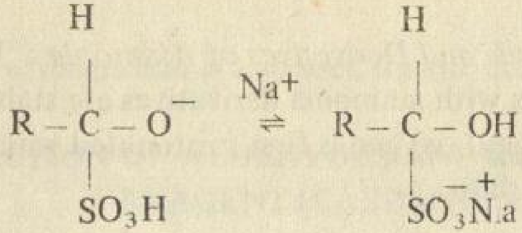
α - hydroxy acid

2. ADDITION OF SODIUM BISULPHITE

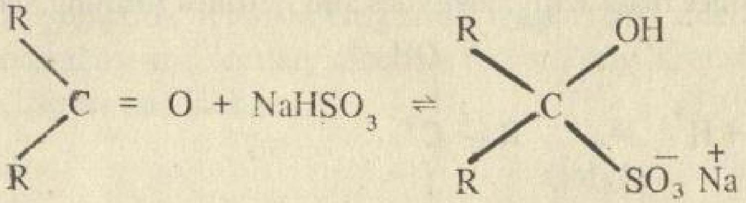
Aldehydes and methyl ketones react with a saturated aqueous solution of sodium bisulphite to form solid crystalline addition compounds known as "bisulphite addition compound." Here bisulphite attacks electrophilic carbon of carbonyl group and then the migration of proton takes place to the carbonyl oxygen.



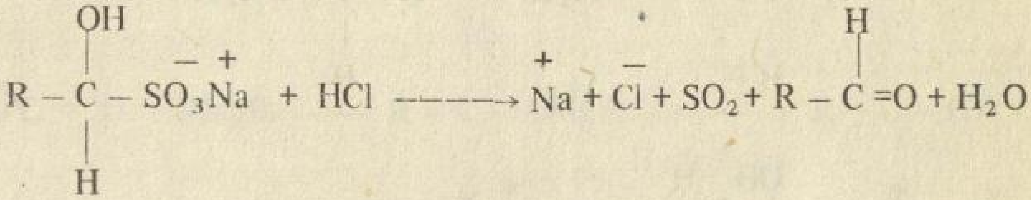
$$R-\overset{H}{\overset{|}{C}}\overset{+\delta}{=}\overset{-\delta}{O} + \overset{+}{Na}\,\overset{-}{HSO_3} \rightleftharpoons R-\underset{SO_3H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-O^- + \overset{+}{Na}$$



$$R-\overset{H}{\underset{SO_3H}{C}}-O^- \overset{Na^+}{\rightleftharpoons} R-\overset{H}{\underset{\overset{-}{S}O_3\overset{+}{N}a}{C}}-OH$$



The crystalline bisulphite addition compound regenerate aldehyde or ketone on treatment with mineral acid.



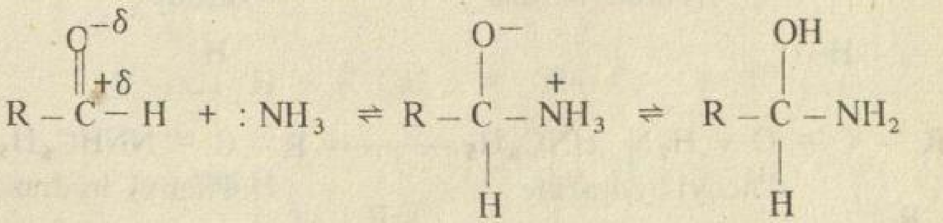
$$R-\overset{OH}{\underset{H}{C}}-\overset{-}{S}O_3\overset{+}{Na} + HCl \longrightarrow \overset{+}{Na} + \overset{-}{Cl} + SO_2 + R-\overset{H}{C}=O + H_2O$$

This reaction is widely used to separate aldehyde or ketone from non-carbonyl compounds. It is to note here that only those ketones undergo this reaction which have at least one methyl group attached to carbonyl carbon.

3. ADDITION REACTIONS WITH AMMONIA AND ITS DERIVATIVES

Ammonia and its derivatives form addition compounds with aldehydes and ketones. All these compounds contain nucleophilic nitrogen which attacks the carbonyl carbon.

(*i*) *Reaction with Ammonia :*



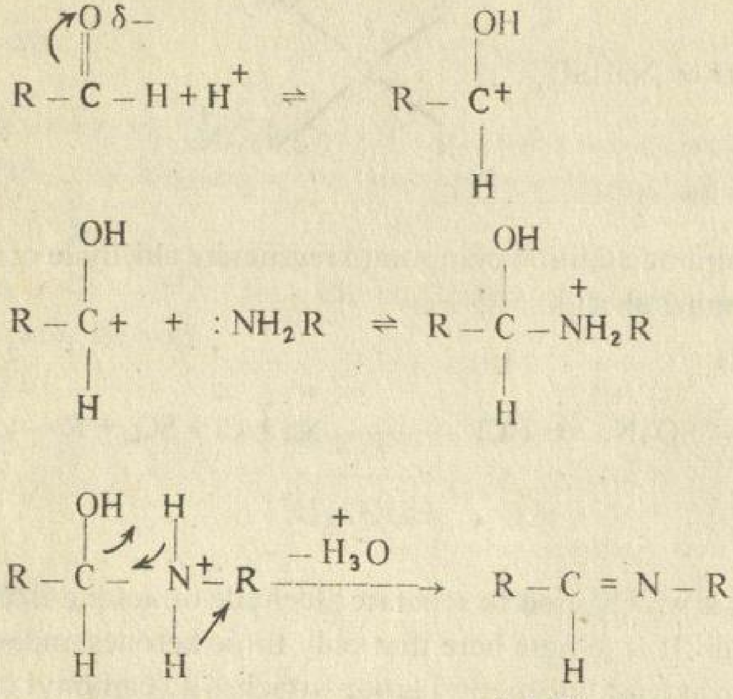
$$R-\overset{O^{-\delta}}{\overset{\|}{C}}{}^{+\delta}-H + :NH_3 \rightleftharpoons R-\overset{O^-}{\underset{H}{C}}-\overset{+}{N}H_3 \rightleftharpoons R-\overset{OH}{\underset{H}{C}}-NH_2$$

Aldehyde — Aldehyde Ammonia

The addition compounds of aldehydes and ketones with ammonia are unstable and undergo dehydration and then polymerisation.

(*ii*) *Reaction with Ammonia and Derivatives of Ammonia* : Reaction products of aldehydes and ketones with ammonia derivatives are stable. These reactions are acid catalysed. Carbonyl oxygen is first protonated which increase the electrophilicity of carbonyl carbon.

(*a*) Primary amines react with aldehydes and ketones forming Schiff's bases :



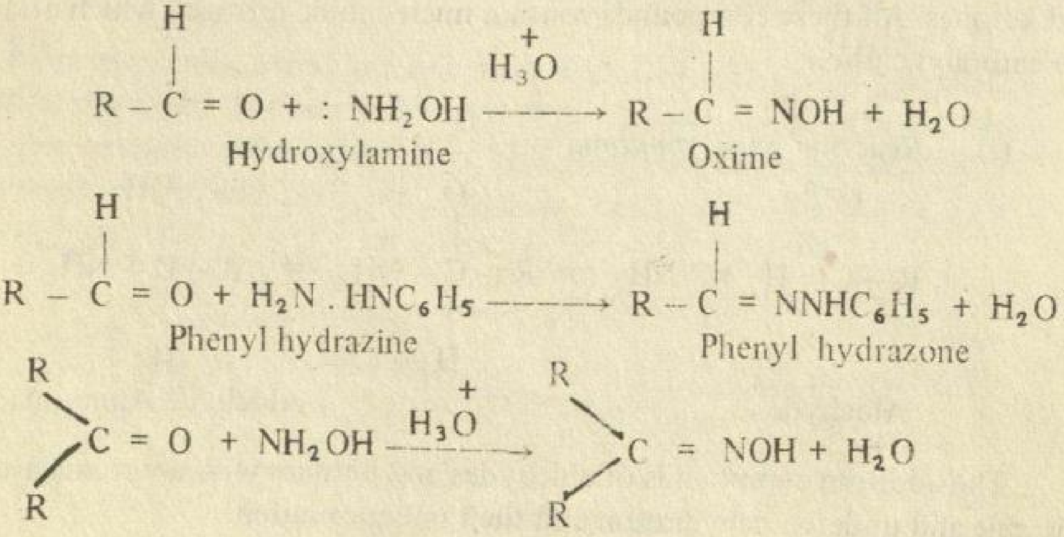
$$R-\overset{\overset{O\,\delta-}{\|}}{C}-H+\overset{+}{H} \rightleftharpoons R-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C^{+}}}$$

$$R-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}+ \;+\; :NH_2R \rightleftharpoons R-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-\overset{+}{N}H_2R$$

$$R-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{\overset{+}{N}}}-R \xrightarrow{-\overset{+}{H_3O}} R-\underset{\underset{H}{|}}{C}=N-R$$

Schiff's base

(*b*) The reaction products of aldehydes and ketones with hydroxyl amine and phenyl hydrazine are solid *oximes* and *phenylhydrazones,* respectively. These products are important because they are often used to identify and purify aldehydes and ketones.



$$R-\overset{\overset{H}{|}}{C}=O+:NH_2OH \xrightarrow{\overset{+}{H_3O}} R-\overset{\overset{H}{|}}{C}=NOH+H_2O$$

Hydroxylamine Oxime

$$R-\overset{\overset{H}{|}}{C}=O+H_2N\,.\,HNC_6H_5 \longrightarrow R-\overset{\overset{H}{|}}{C}=NNHC_6H_5+H_2O$$

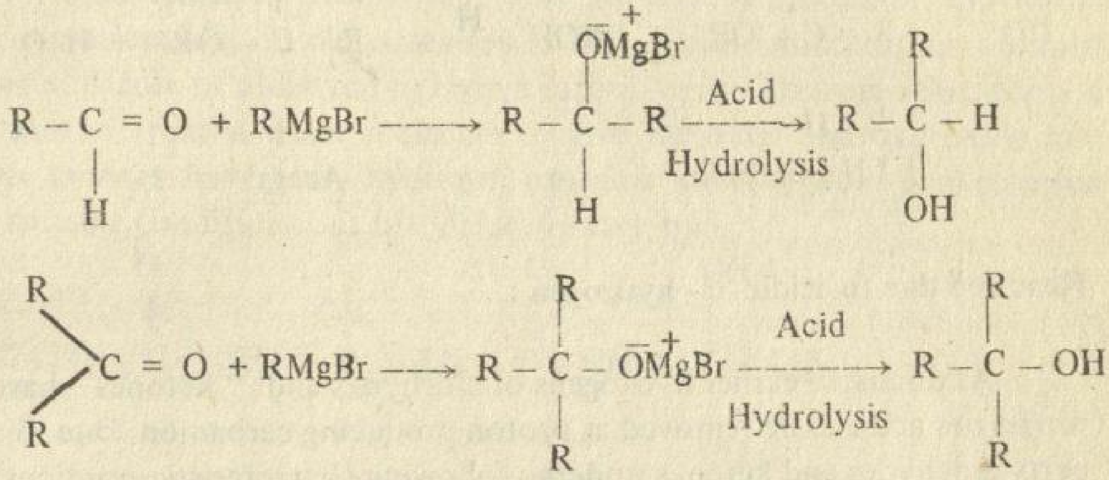
Phenyl hydrazine Phenyl hydrazone

$$\genfrac{}{}{0pt}{}{R}{R}\!\!>C=O+NH_2OH \xrightarrow{\overset{+}{H_3O}} \genfrac{}{}{0pt}{}{R}{R}\!\!>C=NOH+H_2O$$

Oxime formation is also used for the estimation of aldehydes and ketone.

4. REACTION OF ALDEHYDES AND KETONES WITH GRIGNARD'S REAGENT (CARBANION ADDITIONS)

The reaction between Grignard's reagent and aldehydes or ketones to form secondary and tertiary alcohols respectively have already been discussed in the chapter on alcohols.

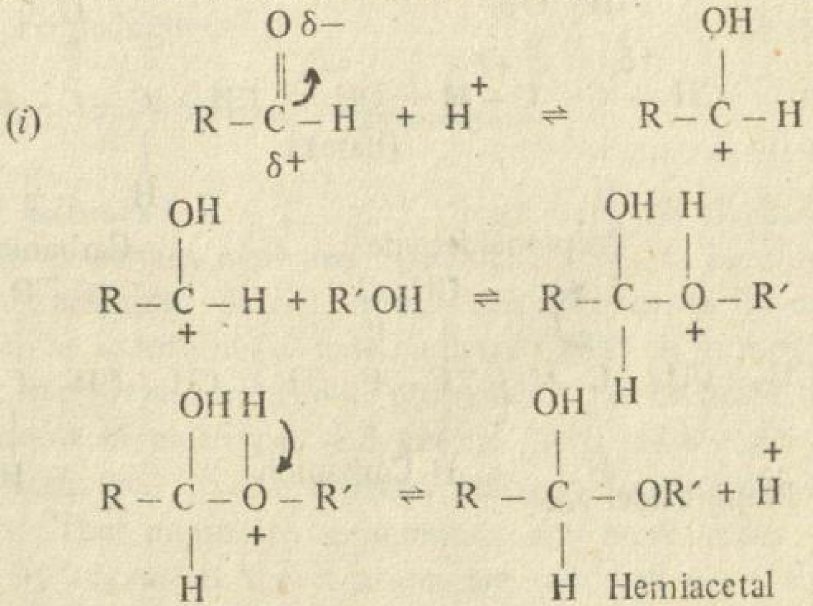


$$R-\underset{H}{C}=O + RMgBr \longrightarrow R-\overset{\bar{O}\overset{+}{Mg}Br}{\underset{H}{C}}-R \xrightarrow[\text{Hydrolysis}]{\text{Acid}} R-\overset{R}{\underset{OH}{C}}-H$$

$$\overset{R}{\underset{R}{>}}C=O + RMgBr \longrightarrow R-\overset{R}{\underset{R}{C}}-\bar{O}\overset{+}{Mg}Br \xrightarrow[\text{Hydrolysis}]{\text{Acid}} R-\overset{R}{\underset{R}{C}}-OH$$

5. REACTION WITH ALCOHOLS (ADDITION OF ALCOHOLS)

Alcohols add to carbonyl group of aldehydes only to form hemiacetal and acetals. The reaction takes place in the presence of anhydrous hydrochloric acid which acts as a catalyst. Hemiacetals are characterized by a carbon atom which is linked to a hydroxyl and an ether group, where as acetals have a carbon atom which is linked to two ether groups.



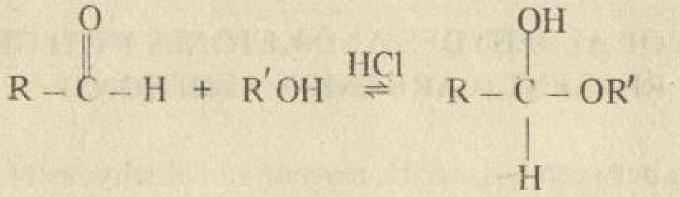
(*i*) $$R-\overset{O\,\delta-}{\underset{\delta+}{\overset{\|}{C}}}-H + \overset{+}{H} \rightleftharpoons R-\overset{OH}{\underset{+}{C}}-H$$

$$R-\overset{OH}{\underset{+}{C}}-H + R'OH \rightleftharpoons R-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{+}{O}}-R'$$

$$R-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{+}{O}}-R' \rightleftharpoons R-\overset{OH}{\underset{H}{C}}-OR' + \overset{+}{H}$$

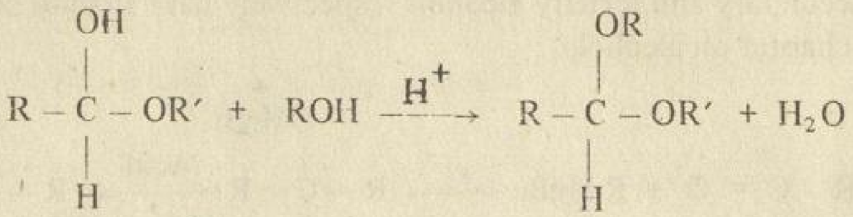
Hemiacetal

The overall reaction may be represented as



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H + R'OH \overset{HCl}{\rightleftharpoons} R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-OR'$$

(*ii*)



$$R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-OR' + ROH \xrightarrow{H^+} R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OR}{|}}{C}}-OR' + H_2O$$

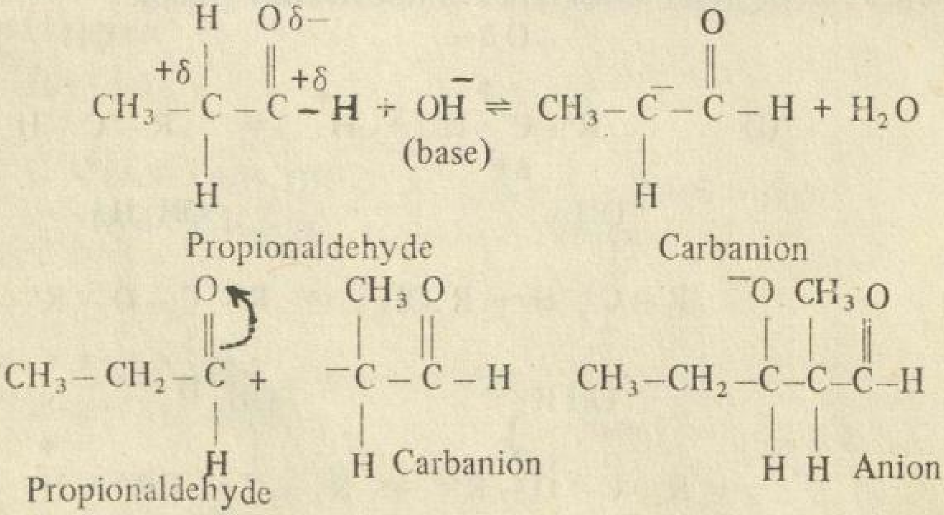
Hemiacetal Acetal

Reaction due to acidic α - hydrogen :

As discussed earlier hydrogens of aldehydes and " ketones" have acidic properties and can be removed as proton producing carbanion. Due to this property aldehydes and ketones undergo following characteristic reactions :

1. *Aldol Condensation* : Aldehydes and ketones possessing α-hydrogens may add to another member in the presence of a dilute base to form condensation product referred to as aldols.

An aldol means a compound which has both aldehydic and an alcoholic group. The reaction is illustrated by the following equations :

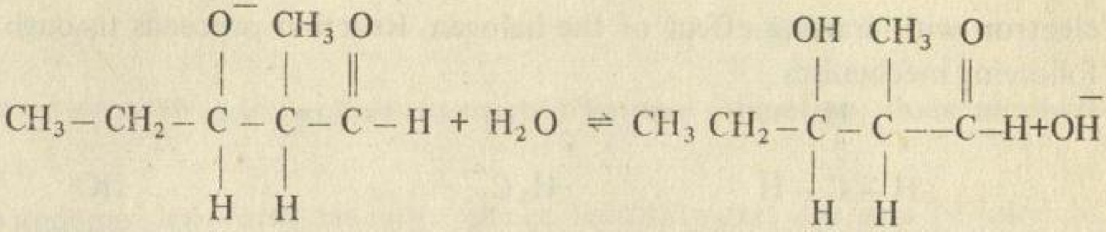


$$CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{\overset{+\delta}{C}}}-\overset{\overset{\displaystyle O\delta-}{\|}}{C}{}^{+\delta}-H + \underset{(base)}{\overline{OH}} \rightleftharpoons CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{-}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-H + H_2O$$

Propionaldehyde Carbanion

$$CH_3-CH_2-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle O}{\|}}{C}} + {}^{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-H \qquad CH_3-CH_2-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle {}^{-}O}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

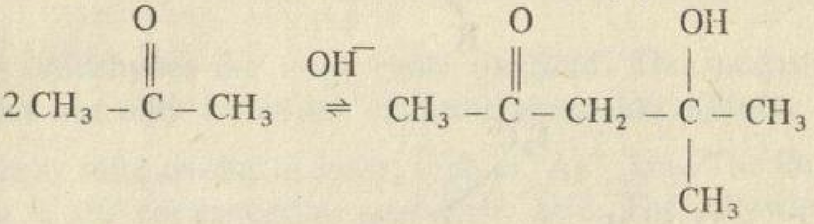
Propionaldehyde Carbanion Anion



$$CH_3-CH_2-\underset{H}{\overset{O^-}{C}}-\underset{H}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-H + H_2O \rightleftharpoons CH_3\,CH_2-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-H+\overline{OH}$$

Anion Aldol

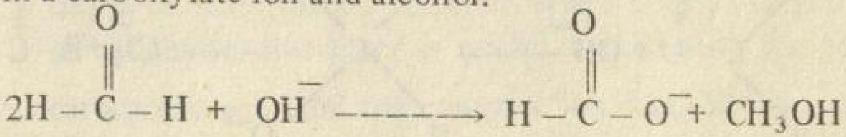
First an aldehyde reacts with base to form a carbanion. Carbanion which is nucleophilic in character reacts with electrophilic carbon atom of another molecule of aldehyde to form a carbon bond. The anion thus formed takes proton from a water molecule to give the aldol and hydroxide ion. Though ketones having α - hydrogen can also undergo aldol condensation under suitable conditions but the yields are very poor.



$$2\,CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \overset{OH^-}{\rightleftharpoons} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\underset{CH_3}{\overset{OH}{C}}-CH_3$$

Cannizaro's Reaction :

Aldehydes having no hydrogen attached to α-carbon do not undergo aldol condensation. Such aldehydes react with conc. aqueous solution of alkali to form a carboxylate ion and alcohol.

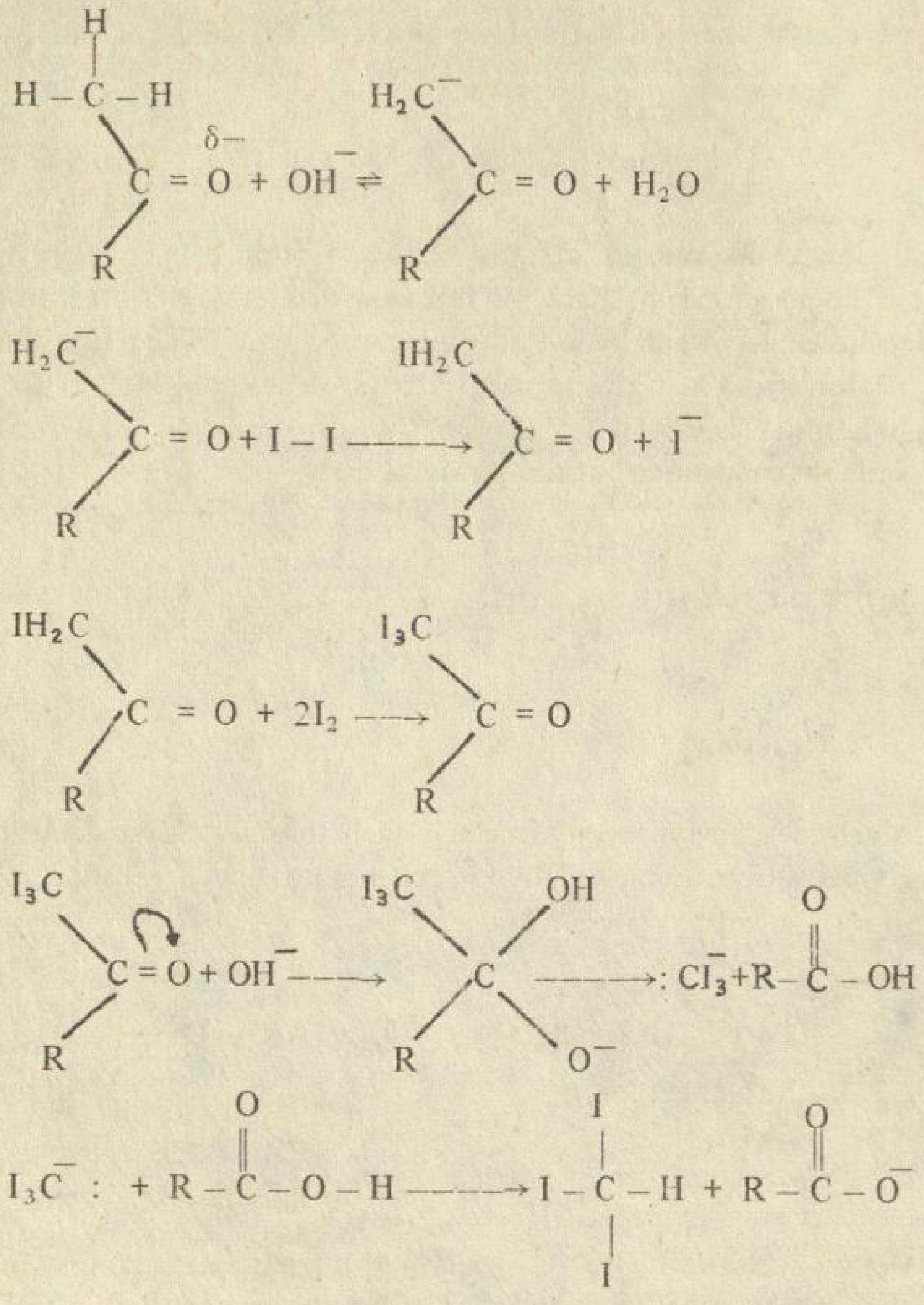


$$2H-\overset{O}{\overset{\|}{C}}-H + \overline{OH} \longrightarrow H-\overset{O}{\overset{\|}{C}}-O^- + CH_3OH$$

Formaldehyde Methyl alcohol

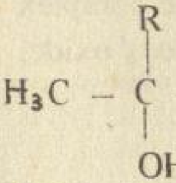
2. *Haloform Reaction – Halogenation :*

Methyl Ketones ($R-\overset{O}{\overset{\|}{C}}-CH_3$) react with the alkaline solution of halogen to form trihalo methanes (HCX_3) known as haloforms. Among aldehydes only acetaldehyde can undergo this reaction. In the case of iodine yellow crystalline iodoform (tri-iodo-methane CHI_3) is formed which has a characteristic odour and anticeptic properties. Due to acidic nature of α-hydrogen atoms in aldehydes and ketones, it is more easily replaced by halogens as compared to the ordinary halogenation in case of saturated hydrocarbons. The monohalo compounds are more easily halogenated because the hydrogens at the α-carbon are rendered more acidic by the electron with-drawing effect of the halogen. Reaction proceeds through the following mechanism.



Iodoform

This reaction is used as a test for the methyl ketone structure, $CH_3-\overset{O}{\overset{\|}{C}}-R$. Since under the conditions of this reaction ethanol is oxidised to acetaldehyde ($CH_3 - \overset{O}{\overset{\|}{C}} - H$) and secondary alcohols with structure


$H_3C-\underset{OH}{\overset{R}{C}}-H$ are oxidised to methyl ketones, therefore, these alcohols also undergo haloform reaction. Hence haloform test can also be used to detect the presence of these alcohols.

Methyl ketones and acetaldehyde will form chloroform ($CHCl_3$) and bromoform ($CHBr_3$) on reaction with chlorine and bromine respectively.

(*c*) *Oxidation and Reduction of Aldehydes and Ketones :*

Oxidation :

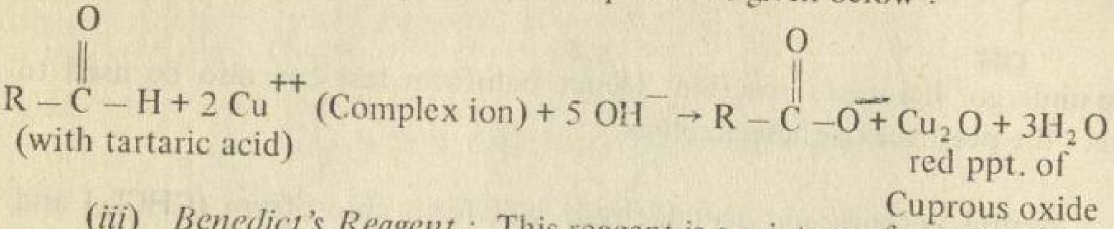
Aldehydes are most easily oxidized. The oxidation can be brought about not only by strong oxidizing agents like $KMnO_4$ and $K_2Cr_2O_7$, but even by mild oxidizing agent, such as Ag^+ ions. The final product of oxidation is the corresponding carboxylic acid. The following are the few mild oxidizing reagents that oxidize aldehydes but not ketones.

(*i*) Tollen's reagent : This reagent contains silver ammonia complex ions, $[Ag(NH_3)_2]^+$ and is prepared by adding ammonium hydroxide to silver nitrate solution. When Tollen's reagent is added to an aldehyde, the latter is readily oxidized to the corresponding carboxylic acid and the complex ion $[Ag(NH_3)_2]^+$ is reduced to metallic silver. If reaction is carried out in a clean test tube the metallic silver is deposited on the walls of the tube in the form of a silver mirror. Therefore this test is also known as the silver mirror test.

$$R-\overset{O}{\overset{\|}{C}}-H + 2\,[Ag(NH_3)_2]^+ + 2\,OH^- \longrightarrow R-\overset{O}{\overset{\|}{C}}-\bar{O} + 2\,Ag + 4NH_3 + 2H_2O$$

(Silver ammonia complex) Metallic silver in the form of mirror.

(*ii*) Fehling's Reagent : This reagent contains sodium hydroxide, cupric sulphate and the sodium salt of tartaric acid. The latter forms a complex with cupric ion and remains dissolved in the solution. This solution has a characteristic deep blue colour. When Fehling's solution is added to an aldehyde, the latter is oxidized to the corresponding carboxylic acid and the complex ion is reduced to a reddish brown precipitate of cuprous oxide. The simplified form of the equation is given below :

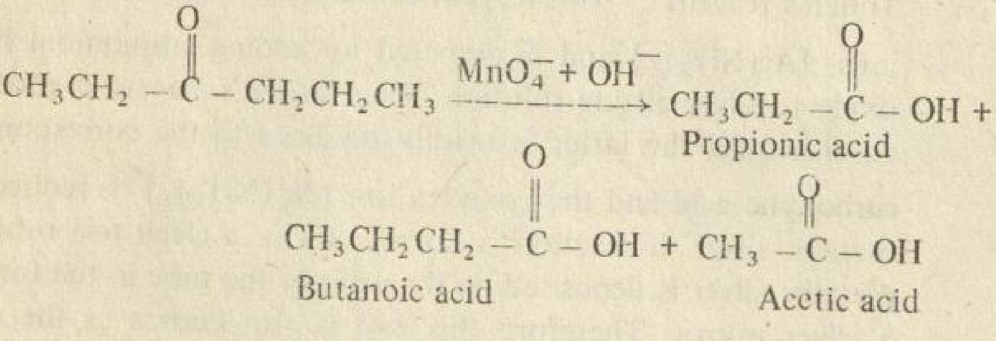


$$\underset{\text{(with tartaric acid)}}{R-\overset{\overset{O}{\|}}{C}-H + 2\,Cu^{++}}\ (\text{Complex ion}) + 5\,OH^{-} \rightarrow R-\overset{\overset{O}{\|}}{C}-O^{-} + \underset{\substack{\text{red ppt. of}\\ \text{Cuprous oxide}}}{Cu_2O} + 3H_2O$$

(*iii*) *Benedict's Reagent :* This reagent is a mixture of cupric sulphate, sodium carbonate, and sodium citrate. The later is used as a complexing agent. The cupric complex ion is soluble in the solution and like Fehling's solution has a deep blue colour. On addition of aldehyde a red brown precipitate of cuprous oxide is formed. The reaction is the same as in Fehling's solution.

Oxidation of Ketones :

Ketones resist oxidation and can be oxidized only by strong oxidizing agents like $KMnO_4$ in an alkaline medium. The carbon bond is broken down with the result that a number of acids are formed. Thus acids have less number of carbon atoms than the original ketone.



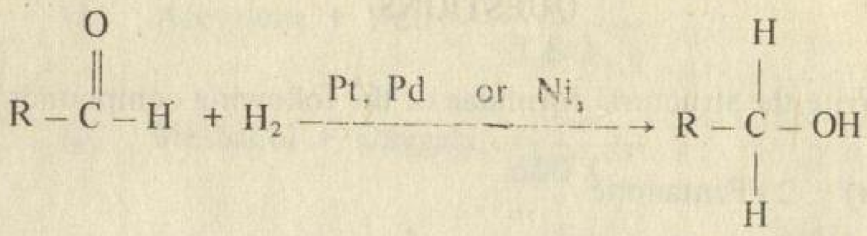
$$CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_2CH_3 \xrightarrow{MnO_4^- + OH^-} \underset{\text{Propionic acid}}{CH_3CH_2-\overset{\overset{O}{\|}}{C}-OH} +$$

$$\underset{\text{Butanoic acid}}{CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{Acetic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH}$$

Ketones cannot be oxidized by mild oxidizing agents like Tollen's reagent or Fehling's solution. This difference in case of oxidation is very important to distinguish between aldehydes and ketones. Ketones do not give silver mirror test and do not reduce Fehling's solution.

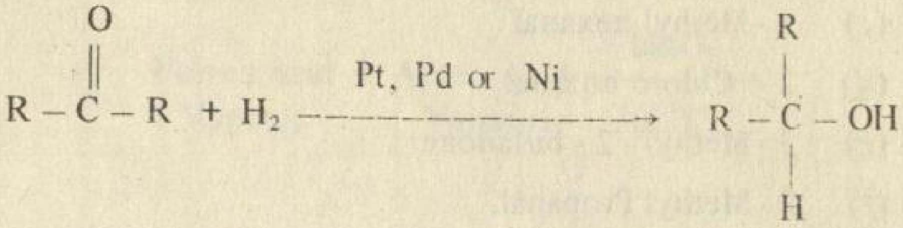
Reduction of Aldehydes and Ketones :

Aldehydes and ketones can be reduced to primary alcohols and secondary alcohols respectively. The reduction is brought about either by catalytic hydrogenation or by use of chemical reducing agents like Lithium Aluminum hydride, $LiAlH_4$.



$$R-\overset{\overset{O}{\|}}{C}-H + H_2 \xrightarrow{Pt,\ Pd\ \text{or}\ Ni,} R-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-OH$$

Primary alcohol

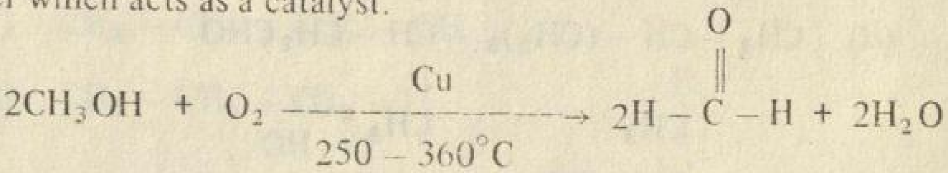


$$R-\overset{\overset{O}{\|}}{C}-R + H_2 \xrightarrow{Pt,\ Pd\ \text{or}\ Ni} R-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}-OH$$

Secondary alcohol

Fomaldehyde ($H-\overset{\overset{O}{\|}}{C}-H$):

Formaldehyde is commercially prepared by the catalytic oxidation of methanol. Methanol in vapour state is mixed with air and passed over hot copper which acts as a catalyst.

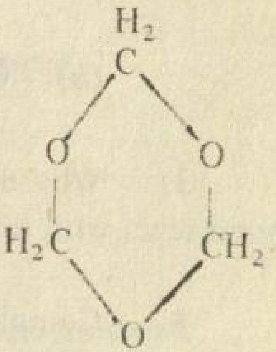


$$2CH_3OH + O_2 \xrightarrow[250-360^\circ C]{Cu} 2H-\overset{\overset{O}{\|}}{C}-H + 2H_2O$$

Formaldehyde is a gas having irritating odour. It is soluble in water and therefore, is generally used in the form of an aqueous solution. Approximately 40% solution of formaldehyde in water is known as formaline. When aqueous solution of formaldehyde is evaporated it forms a solid polymer called para formaldehyde. If the aqueous solution of formaldehyde is heated with dilute sulphuric acid a trimer called trioxane is formed.

$HO(CH_2O)_n\,CH_2OH$

Paraformaldehyde



Trioxane

Uses :

Formaline is used as a preservative for biological specimens. Formaldehyde is mainly used for the production of polymers. One common polymer is known as Bakelite.

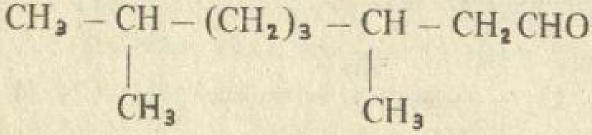
QUESTIONS

1. Write the structural formulae of the following compounds :-

   (*a*) 2 - Pentanone
   (*b*) Pentanal
   (*c*) 3 - Methyl hexanal
   (*d*) 2 - Chloro butanal
   (*e*) 3 - Methyl - 2 - butanone
   (*f*) 2 - Methyl Propanal.

2. Give the IUPAC name to the following compounds :-

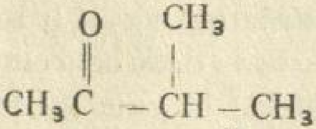
   (*a*) CH_3CH_2CHO
   (*b*) $CH_3(CH_2)_4CHO$
   (*c*) $(CH_3)_2CHCHO$
   (*d*)



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-(CH_2)_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2CHO$$

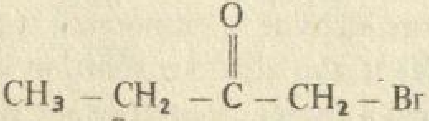
   (*e*) $CH_3-CO-CH_3$
   (*f*

   (*f*)



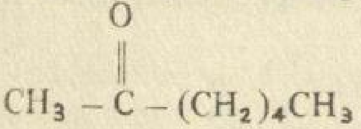
$$CH_3\overset{\displaystyle O}{\overset{\|}{C}}-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_3$$

   (*g*)



$$CH_3-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2-Br$$

   (*h*)



$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_4CH_3$$

3. Why do the carbonyl double bond and the carbon-carbon double bond react with different reagents ? Give reasons.

4. Complete and balance the following reactions :-

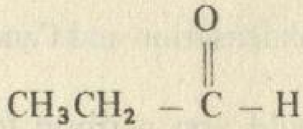
   (*a*) Calcium acetate $\xrightarrow{\text{heat}}$

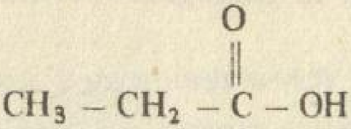
(*b*) Acetylene + Water $\xrightarrow[HgSO_4]{H_2SO_4}$

(*c*) Methanol + Oxygen $\xrightarrow[300^\circ C]{Cu}$

(*d*) Calcium formate + Calcium acetate $\xrightarrow{heat}$

(*e*) $\underset{\text{Vapours}}{\text{Formic acid}} + \underset{\text{Vapours}}{\text{Acetic Acid}} \xrightarrow[300^\circ C]{MnO_2}$

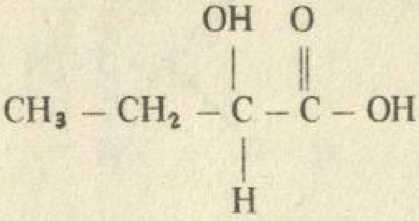
5. How would you convert  $CH_3CH_2-\overset{O}{\overset{\|}{C}}-H$ into the following compounds :

(*a*)  $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH$

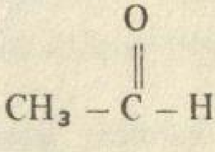
(*b*) $CH_3-HC=CH_2$

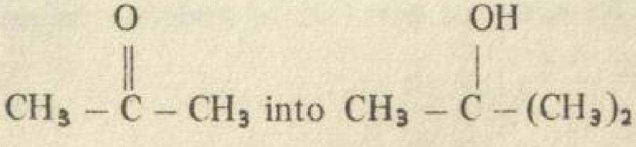
(*c*) $CH_3-CH_2-CH_2-OH$

(*d*) $CH_3-CH_2-CH_2-I$

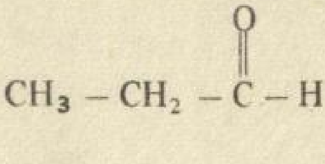
(*e*)  $CH_3-CH_2-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-OH$

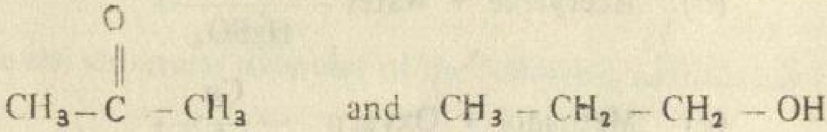
6. How would you convert.

(*a*)  $CH_3-\overset{O}{\overset{\|}{C}}-H$ into $CH_3-CH_2-CH(OH)CH_3$

(*b*)  $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ into $CH_3-\overset{OH}{\overset{|}{C}}-(CH_3)_2$

7. How would you proceed to separate the following mixtures :

(*a*)  $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$ and CH_3-CH_2-OH

(b) 

$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ and $CH_3-CH_2-CH_2-OH$

8. What do you understand by the following terms ? Give equations where necessary.

(a) Aldehydes and ketones.

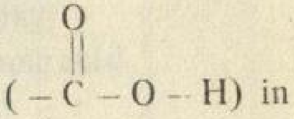
(b) Bromoform reactions and chloroform reactions.

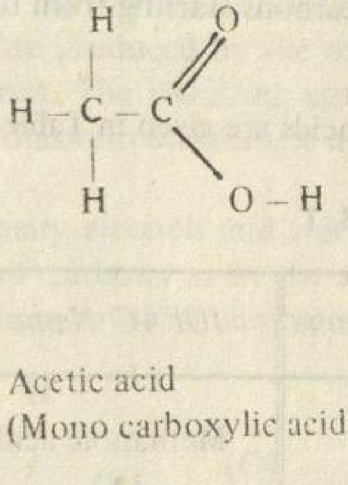
(c) Aldol condensation and Cannizaro's reaction.

9. What tests would you perform to distinguish between acetaldehyde and acetone ? Give reactions.

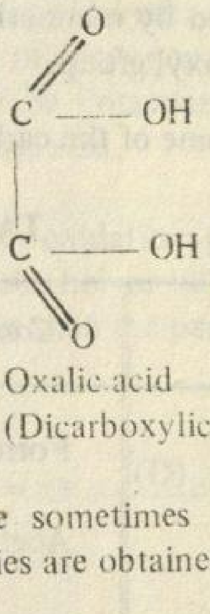
CHAPTER 18

CARBOXYLIC ACIDS

Organic compounds which contain carboxyl group  $(-\overset{\overset{O}{\|}}{C}-O-H)$ in their molecules are known as carboxylic acids. Compounds which contain only one carboxyl group per molecule are known as monocarboxylic acids. While the compounds containing two carboxyl groups per molecule are known as dicarboxylic acids.



Acetic acid
(Mono carboxylic acid)



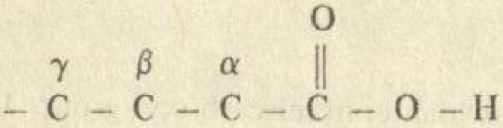
Oxalic acid
(Dicarboxylic acid)

The aliphatic carboxylic acids are sometimes called 'Fatty acid" because certain higher members of the series are obtained from natural fats.

Nomenclature of Carboxylic Acids :

(*i*) *Common System* :– Many carboxylic acids are still called by their common names. These common names have generally been derived from the names of their sources. Formic acid, HCOOH, was first obtained by the distillation of 'Formica' which is a Latin word for ants. The name of acetic acid has been derived from acetum which is a Latin word for vinegar.

The positions of substituents are denoted by using Greek letters α, β, γ etc. The carbon directly attached to carboxyl group is denoted as α, the second carbon as β and so on.



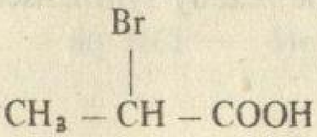
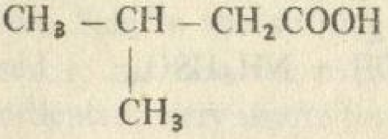
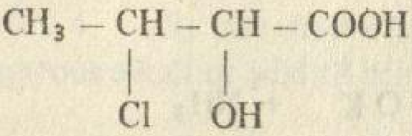
$$-\overset{\gamma}{C}-\overset{\beta}{C}-\overset{\alpha}{C}-\overset{\overset{O}{\|}}{C}-O-H$$

(*ii*) *IUPAC System* : The longest straight chain containing carboxyl group is chosen. The ending – *e* of the name of alkane containing same number of carbon atoms as in the longest chain of carboxylic acid is replaced by -*oic acid*. The position of substituent is denoted by numbering the carbons starting from the carbon of the carboxyl group.

Examples of some of the carboxylic acids are given in Table 18.1.

TABLE 18.1

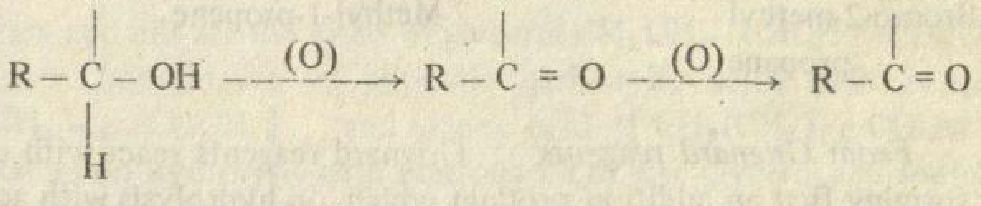
Formula	*Common Name*	*IUPAC Name*	*B. P.*
HCOOH	Formic acid	Methanoic acid	100.7
$CH_3 - COOH$	Acetic Acid	Ethanoic acid	118.1
$CH_3 - CH_2COOH$	Propionic acid	Propanoic acid	141.1
$CH_3 - CH_2 - CH_2COOH$	*n* - Butyric acid	Butanoic acid	163.5

Formula	*Common Name*	*IUPAC Name*	*B. P.*
 $CH_3-\overset{\overset{Br}{\vert}}{C}H-COOH$	α - Bromo-propionic acid.	2-Bromo-propanoic acid.	
 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CH_2COOH$	β - Methyl-butyric acid	3 - Methyl butanoic acid	
 $CH_3-\underset{\underset{Cl}{\vert}}{CH}-\underset{\underset{OH}{\vert}}{CH}-COOH$	β - Chloro -α -hydroxy butyric acid	3-Chloro-2-hydroxy butanoic acid.	

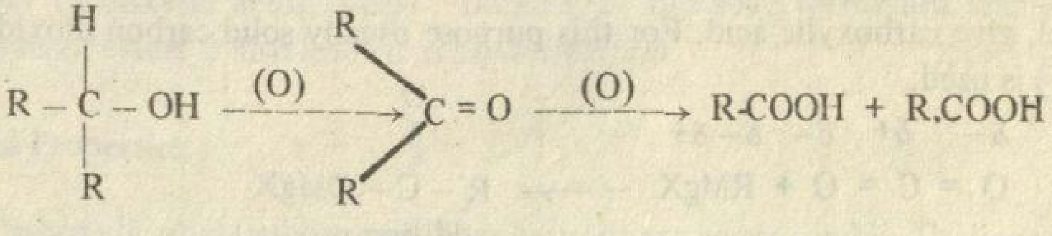
General Methods of Preparation :

1. *By the oxidation of Alcohols, Aldehydes and Ketones :* Carboxylic acids are produced by the oxidation of corresponding alcohols, aldehydes and ketones. The oxidizing agents may be Potassium Permanganate, Nitric acid, or Potassium dichromate in Sulphuric acid.

Primary alcohols and aldehydes, on oxidation, give acids with the same number of carbons as in the starting alcohol or aldehyde. Acids obtained from ketones have less number of carbons than the parent substance.

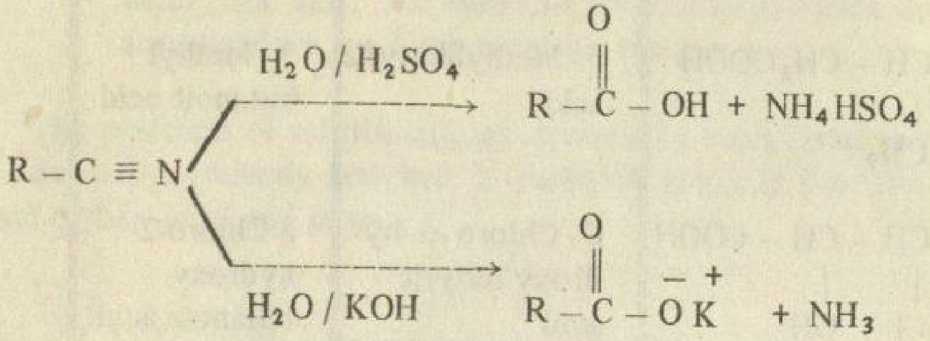


$$R-\overset{\overset{H}{\vert}}{\underset{\underset{H}{\vert}}{C}}-OH \xrightarrow{(O)} R-\overset{\overset{H}{\vert}}{C}=O \xrightarrow{(O)} R-\overset{\overset{OH}{\vert}}{C}=O$$



2. *By the Hydrolysis of Cyanides or Nitriles (Nitrile Synthesis)* : In the presence of an aqueous acid or alkali the hydrolysis of an organic cyanide produces a carboxylic acid. An organic cyanide may be readily synthesised from an alkyl halide and sodium cyanide.

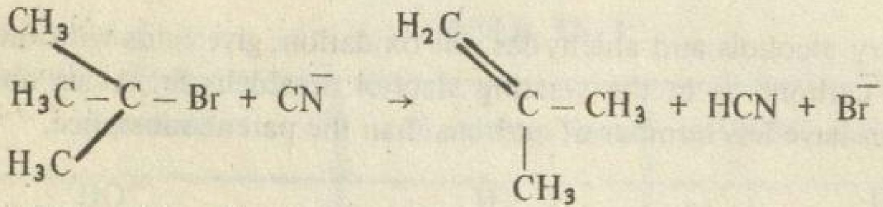
$$R-X + \overset{+}{Na}\overset{-}{CN} \longrightarrow R-CN + \overset{+}{Na}\overset{-}{X}$$



$$R-C\equiv N \xrightarrow{H_2O\,/\,H_2SO_4} R-\overset{\overset{O}{\|}}{C}-OH + NH_4HSO_4$$

$$R-C\equiv N \xrightarrow[H_2O\,/\,KOH]{} R-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{K} + NH_3$$

In presence of acid, nitrogen is liberated as ammonium salt while in presence of alkali it is liberated as free ammonia. This method gives a carboxylic acid with one more carbon atom than was present in the halide. Therefore, this method is used to increase the number of carbon atoms in the chain. This method is one of synthetic importance only in case of primary alkyl halides. Yields of alkyl cyanides from secondary and especially from tertiary alkyl halides are very poor due to elimination reactions producing alkenes as by products.



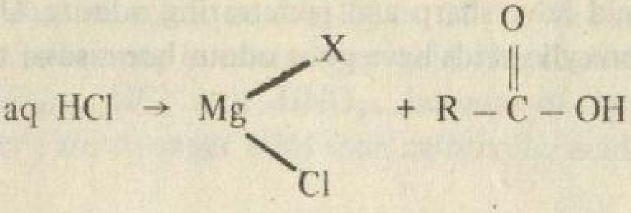
2-Bromo-2-methyl propane

2-Methyl-1-propene

3. *From Grignard reagents* : Grignard reagents react with carbon dioxide forming first an addition product which, on hydrolysis with aqueous acid, give carboxylic acid. For this purpose usually solid carbon dioxide (dry ice) is used.

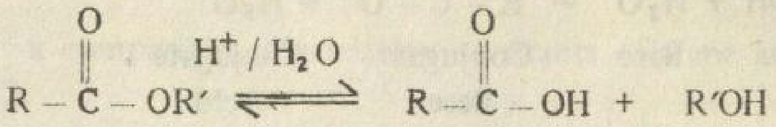
$$\overset{\delta-}{O} = \overset{\delta+}{C} = \overset{\delta-}{O} + \overset{\delta-}{R}\overset{\delta+}{MgX} \longrightarrow R-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{MgX}$$

addition product

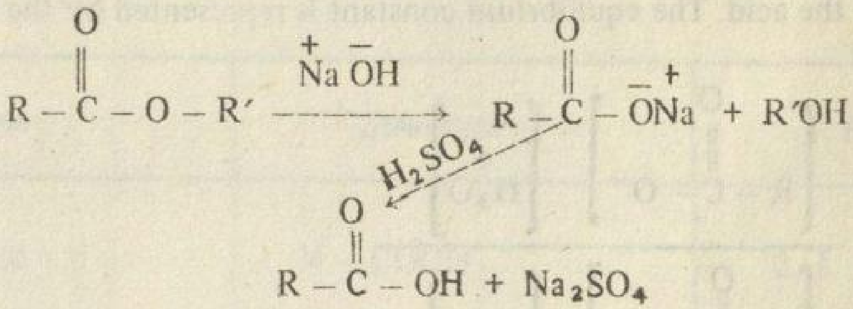


The carboxylic acid prepared by this method has one more carbon atom than in the starting alkyl halide. Therefore this method may also be used to increase the number of carbon atoms in the chain. This method is particularly very useful for converting tertiary halides into carboxylic acid.

4. *By the Hydrolysis of Esters* : Esters may be hydrolysed, with aqueous alkali or acid to acids and alcohols.



$$R-\overset{\overset{O}{\|}}{C}-OR' \xrightleftharpoons{H^+/H_2O} R-\overset{\overset{O}{\|}}{C}-OH + R'OH$$



$$R-\overset{\overset{O}{\|}}{C}-O-R' \xrightarrow{\overset{+}{Na}\overset{-}{OH}} R-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{Na} + R'OH \xrightarrow{H_2SO_4} R-\overset{\overset{O}{\|}}{C}-OH + Na_2SO_4$$

When the hydrolysis is carried out with aqueous alkali, the product is the alkali salt of the corresponding acid from which free acid can be obtained by treating it with some mineral acid.

Fats and oils are the esters of glycerol $CH_2OH - CHOH - CH_2OH$ and the higher homologues of aliphatic carboxylic acids such as palmitic $[CH_3(CH_2)_{14}\ COOH]$, and stearic acid $[CH_3(CH_2)_{16}\ COOH]$ etc. These esters on hydrolysis with equeous alkali give glycerol and sodium salts of higher carboxylic acids (soap). Because of the soap formation alkaline hydrolysis of esters is also known as *saponification*.

Physical Properties :

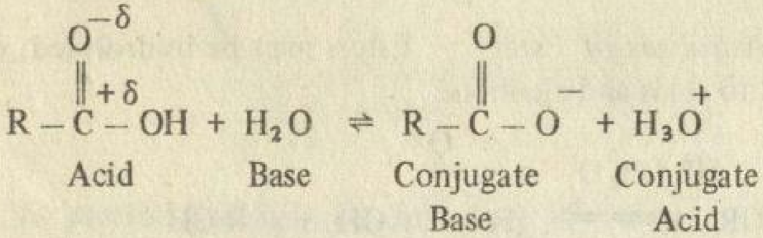
Carboxylic acids having upto four carbons are water soluble. Carboxylic acid with five carbons is partly soluble in water while the higher acids are insoluble in water.

Formic acid and acetic acid have sharp and penetrating odours. Other low molecular weight monocarboxylic acids have poor odour because of their low volatility (higher b.p.)

Chemical Properties

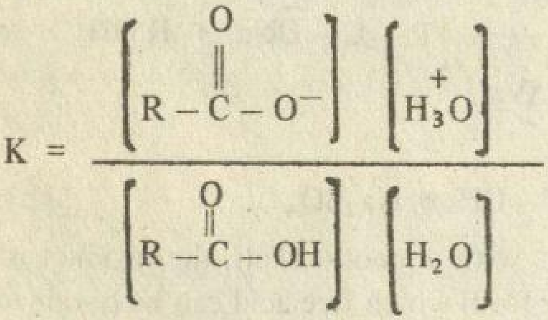
When a carboxylic acid is dissolved in water, it donates a proton to water and forms a carboxylate ion.

Water, which accepts a proton, acts as a base.



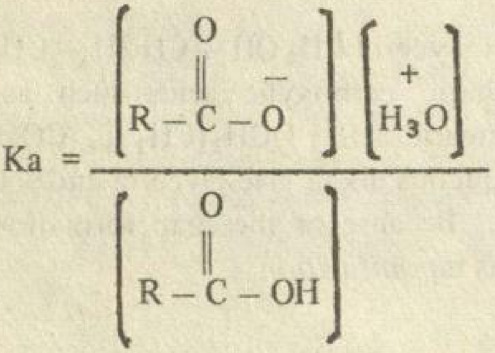
$$\underset{\text{Acid}}{R-\overset{\overset{O^{-\delta}}{\|}}{C}{}^{+\delta}-OH} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Conjugate Base}}{R-\overset{\overset{O}{\|}}{C}-O^{-}} + \underset{\text{Conjugate Acid}}{H_3\overset{+}{O}}$$

The extent to which the equilibrium is shifted towards the right shows the strength of the acid. The equilibrium constant is represented by the following expression :



$$K = \frac{\left[R-\overset{\overset{O}{\|}}{C}-O^{-}\right]\left[H_3\overset{+}{O}\right]}{\left[R-\overset{\overset{O}{\|}}{C}-OH\right]\left[H_2O\right]}$$

The concentration of water, which is present in excess, remains constant,

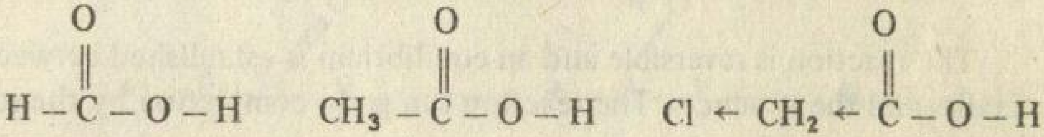


$$Ka = \frac{\left[R-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\right]\left[H_3\overset{+}{O}\right]}{\left[R-\overset{\overset{O}{\|}}{C}-OH\right]}$$

Ka is called ionisation constant or dissociation constant of the acid. The greater the numerical value of the dissociation constant, the stronger is the acid to which it refers. The ionisation constant of formic acid is 2.1×10^{-4}

and that of acetic acid is 1.8×10^{-5}. Formic acid, which has greater ionisation constant, is a stronger acid than acetic acid. Inorganic acids such as H_2SO_4 , HCl and HNO_3, because of their almost complete ionisation in water , are stronger acids than carboxylic acids.

As pointed out earlier acidity of carboxyl group is due to electron attracting nature of carbonyl group. Therefore, it may be concluded that attachment of electron donating group like alkyl group with the carbonyl group will decrease the acidity of acid while electron attracting group like halogen will increase the acidity.



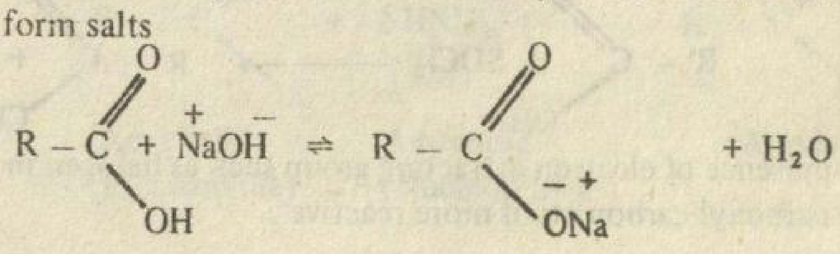
$$H-\overset{\overset{O}{\|}}{C}-O-H \qquad CH_3-\overset{\overset{O}{\|}}{C}-O-H \qquad Cl \leftarrow CH_2 \leftarrow \overset{\overset{O}{\|}}{C}-O-H$$

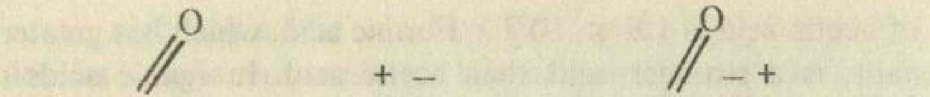
For a comparison, dissociation constants of some acids are given in Table 18.2.

TABLE 18.2

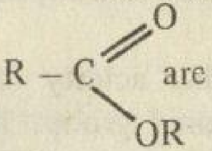
Name	*Structure*	*Ka*
Formic acid	$H-COOH$	2.1×10^{-4}
Acetic acid	$CH_3 \rightarrow COOH$	1.75×10^{-5}
Propionic acid	$CH_3 \rightarrow CH_2 \rightarrow COOH$	1.3×10^{-5}
Chloroacetic acid	$Cl \leftarrow CH_2 \leftarrow COOH$	150×10^{-5}
Fluoroacetic acid	$F \leftarrow CH_2 \leftarrow COOH$	220×10^{-5}

2. *Formation of Salts* : Carboxylic acids react with aqueous alkalie and form salts



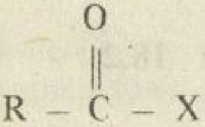


Sodium acetate

3. *Formation of Esters :*  are formed by the reactions of carboxylic acids and alcohols. This reaction is called esterification. It is acid catalysed. The mechanism of esterification is given on page (291).

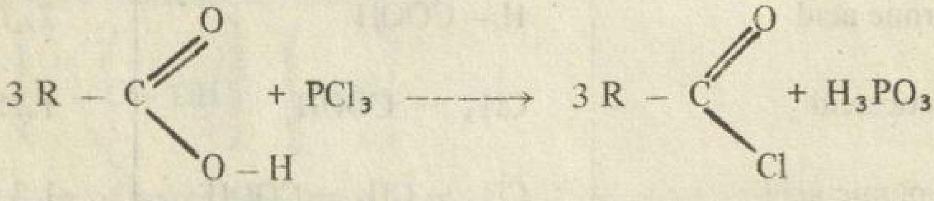
The reaction is reversible and an equilibrium is established between the reactants and the products. The reaction can go to completion by the removal of water as it is produced.

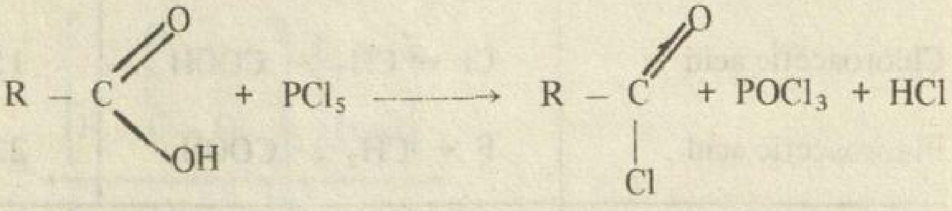
4. *Formation of Acyl Halides or Acid Halides :*

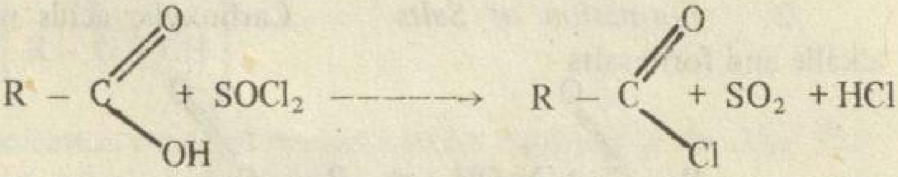


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-X$$

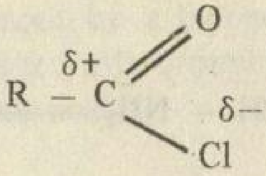
Acyl halides are a group of compounds obtained by the replacement of hydroxyl group of the acid by halogens. The reagents most commonly used for this reaction are phosphorus halides (PCl_3, PCl_5) and thionyl chloride $SOCl_2$.



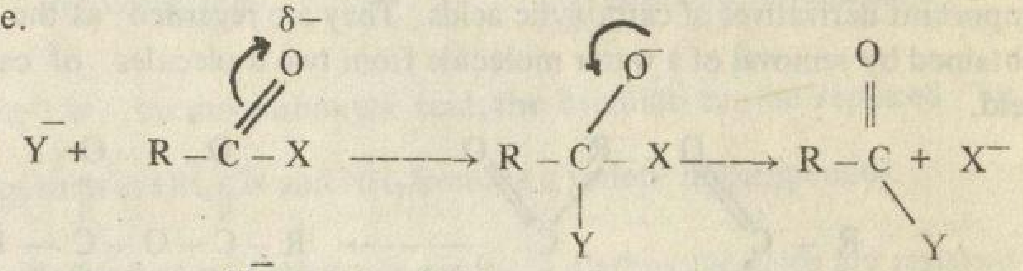




The presence of electron attracting group such as halogen in the acyl halide makes the carbonyl carbon atom more reactive .

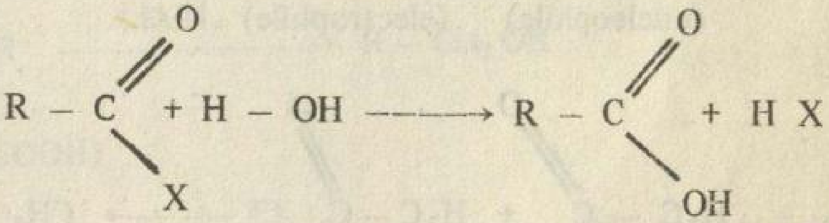


The positive charge on the carbon of carbonyl group is increased and the carbonyl carbon atom becomes more susceptible to the attack of a nucleophilic reagent . The halogen of the acyl halide thus gets readily replaced by a nucleophile.

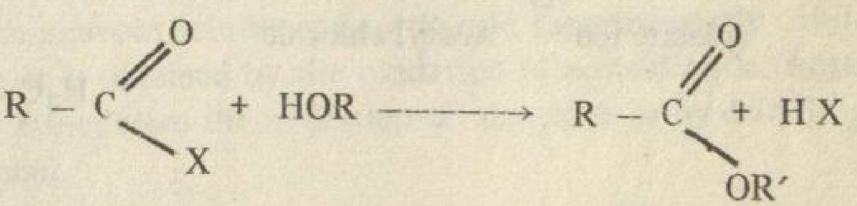


($\bar{Y}$ = nucleophile)

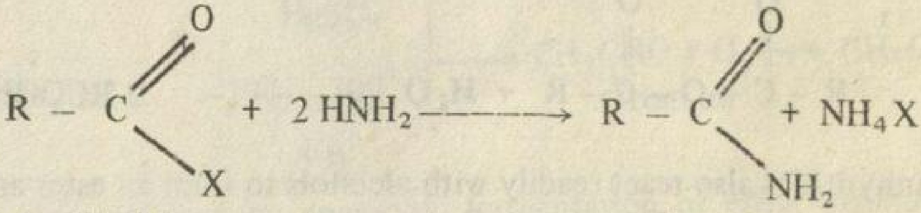
For example acyl halides, on hydrolysis, form acids.



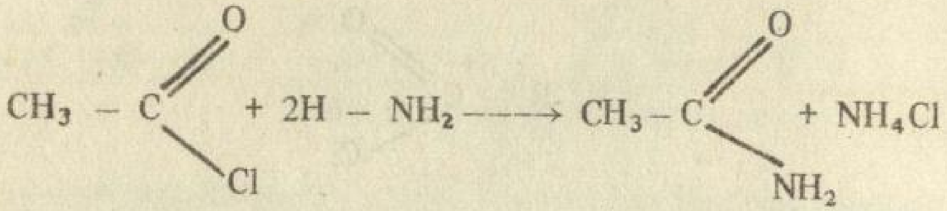
Acyl halides react with alcohols and ammonia to form esters and amides, respectively.



Acyl halide (Electrophile) | Alcohol (Nucleophile) | Ester

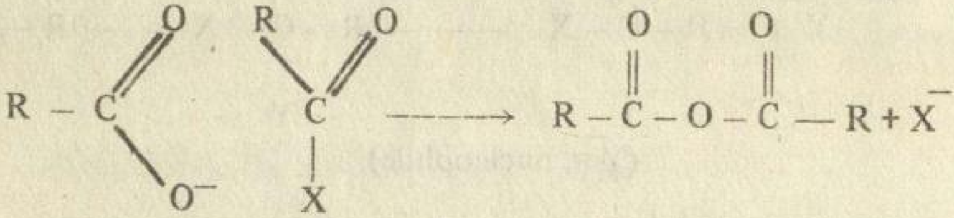


Acyl halide (Electrophile) | Ammonia (Nucleophile) | Amide

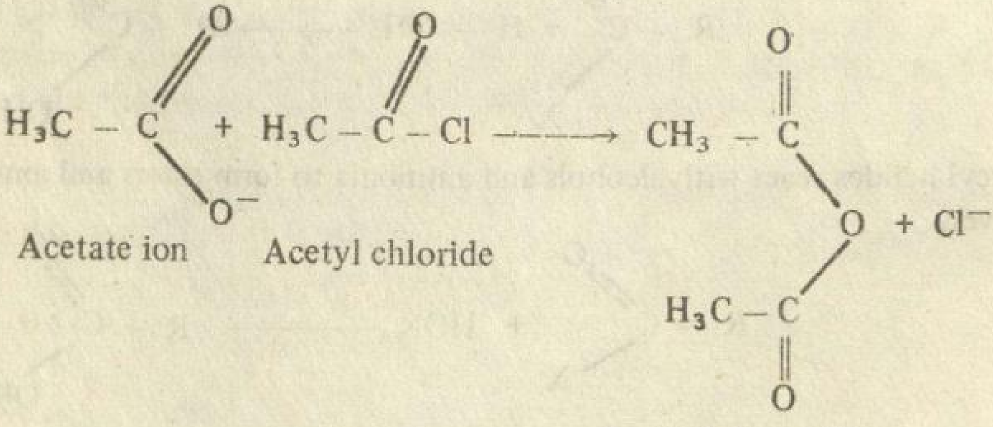


Acetamide

With carboxylate ion acyl halides form *acid anhydrides*. Acid anhydrides are important derivatives of carboxylic acids. They are regarded as the products obtained by removal of a water molecule from two molecules of carboxylic acid.



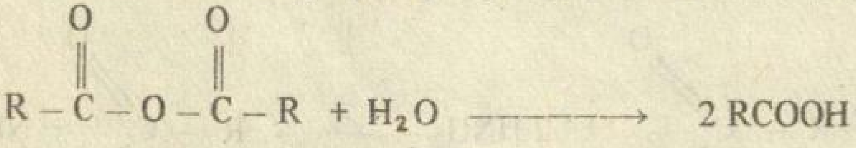
Carboxylate (nucleophile) Acyl halide (electrophile) Acid anhydride



Acetate ion Acetyl chloride

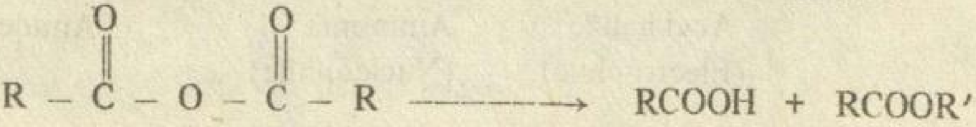
Acetic anhydride

Acid anhydrides are readily hydrolysed into two molecules of acids.



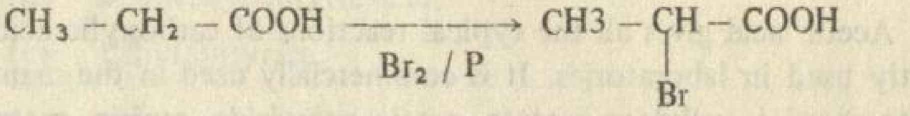
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-R + H_2O \longrightarrow 2\,RCOOH$$

Anhydrides also react readily with alcohols to form an ester and an acid.



$$\underset{+\,R'-OH}{R-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-R} \longrightarrow RCOOH + RCOOR'$$

5. *Formation of α - halogen acids* :- The α - hydrogen atom in carboxylic acids may be replaced by a halogen in presence of a catalyst. Carboxylic acid can be brominated with bromine in the presence of phosphorus to form α - bromo carboxylic acid.



$$CH_3-CH_2-COOH \xrightarrow[Br_2\,/\,P]{} CH3-\underset{\underset{Br}{|}}{CH}-COOH$$

Propionic acid α - Bromo propionic acid

In the α - bromo carboxylic acid, the bromine can be replaced by nucleophiles such as $\overline{OH}$, $\overline{CN}$ and $\overline{NH_2}$ forming a variety of compounds.

6. *Reduction of Carboxylic acids* : - Carboxylic acids are resistant to catalytic hydrogenation. However, carboxylic acids can be reduced to primary alcohols by lithium aluminum hydride ($LiAlH_4$).

$$RCOOH \xrightarrow{LiAlH_4} R-CH_2OH$$

Acetic Acid (CH_3COOH)

Acetic acid is one of the most important monocarboxylic acid and has been known since earliest times. It has been used since old days as vinegar, Vinegar is a dilute aqueous solution of acetic acid (approximately 5%). On commercial scale it is obtained by the oxidation of acetaldehyde. Acetaldehyde is obtained either from the hydration of acetylene or by dehydrogenation of ethyl alcohol.

$$\left.\begin{array}{l} HC \equiv CH \xrightarrow[HgSO_4]{H_2O,\,H_2SO_4} \\ CH_3CH_2OH \xrightarrow[Cu]{290-300^\circ} \end{array}\right] \longrightarrow CH_3CHO + \underset{\text{(from air)}}{O_2} \longrightarrow CH_3COOH$$

Vinegar is also obtained by anaerobic fermentation of ethyl alcohol solution in the presence of bacteria (Azetobacter).

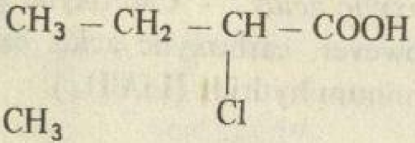
Acetic acid is a colourless liquid (b.p. 118°C) with a pungent odour. It is miscible with water in all proportions. Pure acetic acid is called glacial acetic acid as it solidifies at 16.6°C forming an ice like mass. Acetic acid blisters the skin.

Acetic acid gives all the typical reactions of carboxylic acids. It is frequently used in laboratories. It is commercially used in the manufacture of acetate plastics, cellulose acetate, acetic anhydride, aspirin, metallic acetate etc.

QUESTIONS

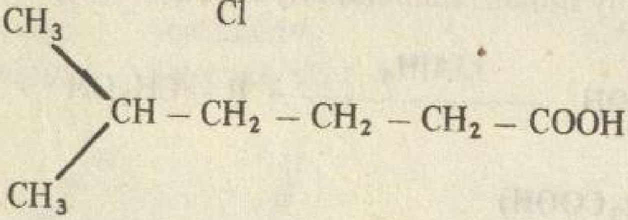
1. Write a correct name for each of the following :

(*a*)

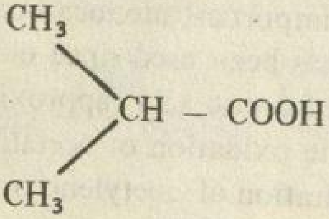


$CH_3-CH_2-\underset{Cl}{\underset{|}{CH}}-COOH$

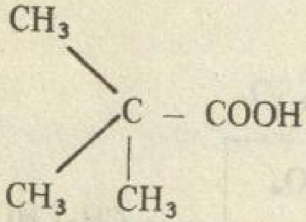
(*b*)



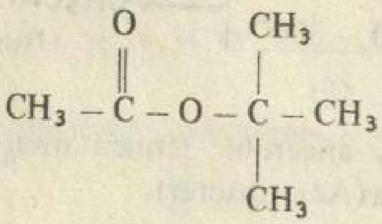
(*c*)



(*d*)



(*e*)



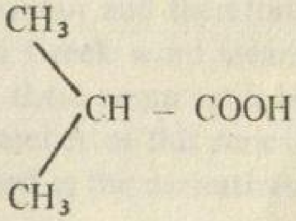
$CH_3-\overset{O}{\overset{\|}{C}}-O-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$

2. Write a structural formula for each of the following :

   (*a*) 2 – Methyl hexanoic acid.
   (*b*) Acetic anhydride.
   (*c*) Sodium propionate.
   (*d*) β - methyl butyric acid.
   (*e*) Ethyl butyrate.

3. Which is a stronger acid in each of the following pairs and why ?

   (*a*) HCl and HCOOH
   (*b*) HCOOH and CH_3COOH
   (*c*) H_2SO_4 and $CH_3 - CH_2 - COOH$
   (*d*) $F - CH_2COOH$ and $Br - CH_2 - COOH$
   (*e*) $CH_3 - CH_2$ COOH and



4. Illustrate with examples what is :

   (*a*) Esterification.
   (*b*) Hydrolysis.
   (*c*) Ionisation constant.
   (*d*) Alcoholysis.
   (*e*) Ammonolysis.

5. How would you perform the following conversions. Show by means of equations :

   (*a*) Acetyl chloride to ethyl acetate.
   (*b*) Methyl chloride to acetic acid.
   (*c*) Acetic acid to acetic anhydride.

(*d*) n Butyl alcohol to *n* - Butyric acid.

(*e*) Acetic acid to acetyl chloride.

(*f*) Ethyl chloride to propanoic acid.

(*g*) α-Bromo butyric acid to α-amino butyric acid.

CHAPTER 19

AROMATIC HYDROCARBONS

As mentioned in Chapter 13 the closed chain hydrocarbons are divided into *alicyclic hydrocarbons* and *aromatic hydrocarbons.* Alicyclic hydrocarbons resemble in their properties with aliphatic hydrocarbons while the properties of aromatic hydrocarbons differ very much from those of aliphatic hydrocarbons . Some members of this family which were isolated and examined in the beginning, were of pleasant odour and therefore, they were named as aromatic compounds. 'Aroma' is a Greek word meaning fragrant smell . The name aromatic is still retained for these compounds but the word has lost its original meaning. The simplest member of this series is benzene. The other aromatic compounds may be regarded as the derivatives of benzene

Sources of Aromatic Hydrocarbons :

The major sources of aromatic hydrocarbons are coal and petroleum. Benzene can also be synthesised from acetylene.

1. *From Coal.* When coal is heated at a high temperature in the absence of air, it decomposes and gives four fractions (i) Coal gas (ii) Coal-tar (iii) Ammonical liquor (iv) Coke. This process is known as destructive distillation of coal. Coal-tar is the richest source of benzene. Coke is pure carbon and is used in steel industry and also as a fuel. Coal gas is also mainly used as fuel.

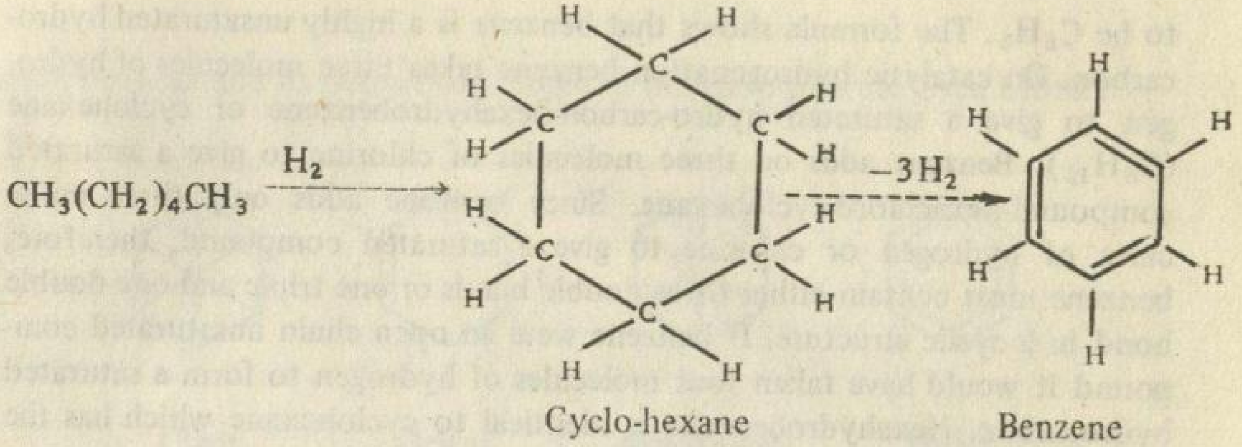
Coal-tar is fractionally distilled and the following fractions are collected (Table 19.1).

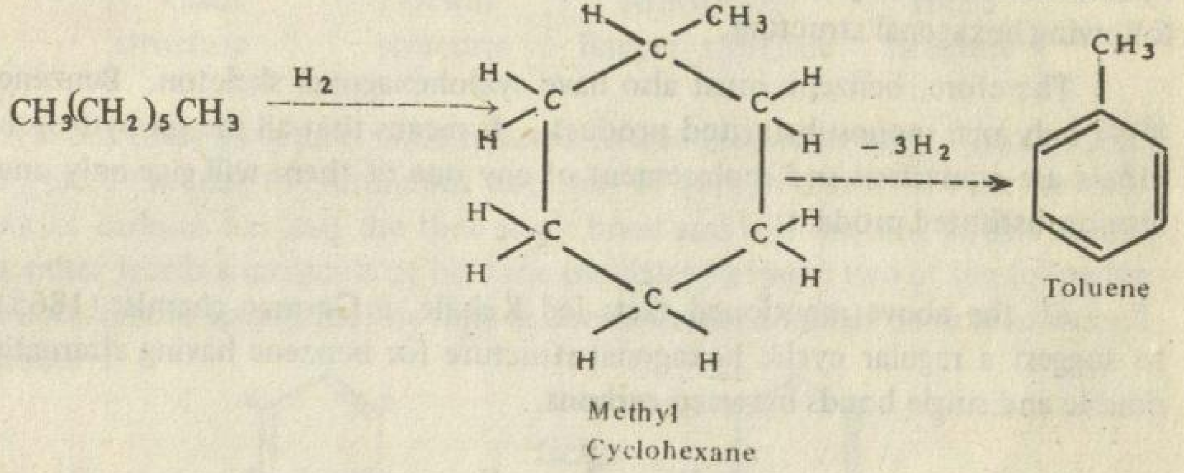
TABLE - 19.1

No.	Name of Fraction	Boiling range° C	Components
1.	Light oil or crude naphtha	70° – 170°	Benzene, toluene, small quantities of aniline and pyridine
2.	Middle oil or carbolic oil	170° – 230°	Phenols, naphthalene and cresols
3.	Heavy oil or creosote oil	230° – 270°	Cresol
4.	Anthracene oil	270° – 360°	Anthracene, phenanthrene etc.

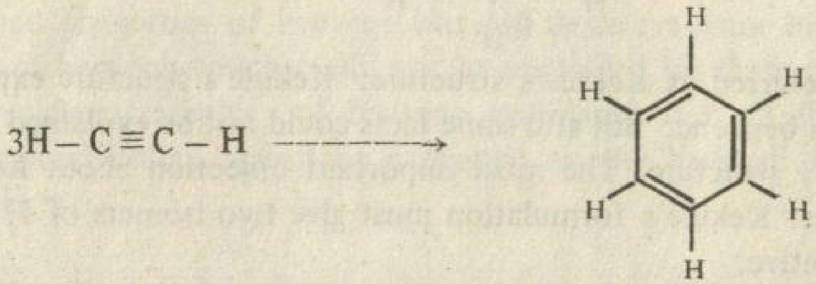
Light oil is further worked out to get benzene and its homologues. One ton of coal may give approximately 120 pounds of coal-tar. Coal-tar contains about 1.6% benzene and about 0.5% homologues of benzene (toluene and xylene). Every year large quantities of coal are destructively distilled to obtain coke for metallurgy and hundred million gallons of benzene.

2. *From Petroleum.* The other important source of benzene is petroleum. As mentioned earlier petroleum is essentially a mixture of alkanes. Alkanes obtained from the refining of petroleum on passing over a platinum catalyst at high temperature and pressure are converted into cycloalkanes which undergo dehydrogenation under the same conditions to give aromatic hydrocarbons. This process is known as *Catalytic reforming* or *hydroformation.* For example *n* - hexane is converted into benzene through formation of cyclohexane while normal heptane gives toluene.


$CH_3(CH_2)_4CH_3$
H_2
$-3H_2$
Cyclo-hexane
Benzene


$CH_3(CH_2)_5CH_3$
H_2
$-3H_2$
Methyl Cyclohexane
Toluene

3. *From Acetylene.* Benzene can also by synthesised by heating acetylene in a closed vessel at a moderately low temperature.


$3H-C\equiv C-H$

Benzene

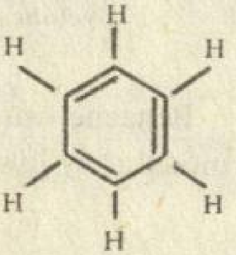
However, this method is not a commercial one and has only theoretical importance. It has been recently reported that in China this method has been commercially exploited.

Structure of Benzene :

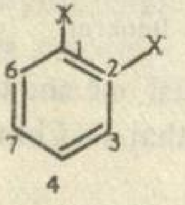
Elucidation of the structure of benzene is an important and interesting problem of organic chemistry. Molecular formula of benzene has been found to be C_6H_6. The formula shows that benzene is a highly unsaturated hydrocarbon. On catalytic hydrogenation benzene takes three molecules of hydrogen to give a saturated hydro-carbon-hexahydrobenzene or cyclohexane (C_6H_{12}). Benzene adds on three molecules of chlorine to give a saturated compound-hexachloro-cyclohexane. Since benzene adds only three molecules of hydrogen or chlorine to give a saturated compound, therefore, benzene must contain either three double bonds or one triple and one double bond in a cyclic structure. If benzene were an open chain unsaturated compound it would have taken four molecules of hydrogen to form a saturated hydrocarbon. Hexahydrobenzene is identical to cyclohexane which has the following hexagonal structure.

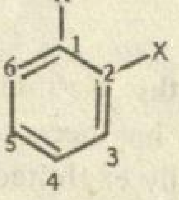
Therefore, benzene must also have cyclohexagonal skeleton. Benzene gives only one monosubstituted product . It means that all the six hydrogen atoms are equivalent and replacement of any one of them will give only one monosubstituted product.

All the above mentioned facts led Kekule, a German chemist (1865) to suggest a regular cyclic hexagonal structure for benzene having alternate double and single bonds between carbons.



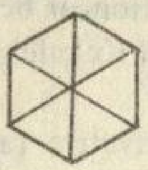
This was referred as Kekule's structure. Kekule's structure explained many facts about benzene. But still some facts could not be explained on the basis of Kekule's structure. The most important objection about Kekule's structure was that Kekule's formulation must give two isomers of 1, 2 - disubstituted derivative.



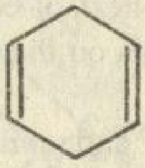


In one isomer the two carbon atoms having two substituents are linked together through a double bond, while in the second isomer these two carbons are linked together through a single bond. But as a matter of fact there is only one 1, 2 disubstituted derivative of benzene.

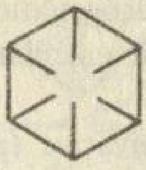
Many other structures of benzene were proposed to explain the properties of benzene and its derivatives. Some of the structures are given below :



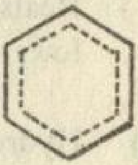
Claus structure



Dewar structure

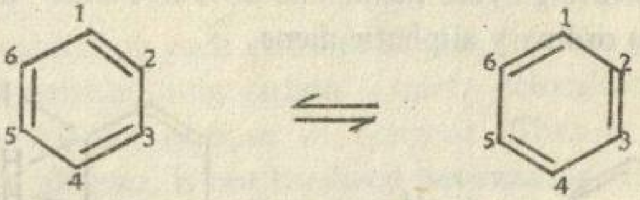


Armstrong-Baeyer structure



Thiele structure

All these structures were rejected on one ground or other. Kekule, then suggested that due to continuous vibration of carbon atoms in benzene each pair of carbons has half the time single bond and half the time double bond. In other words a molecule of benzene oscillates between two of the following structures and spends half its time in one structure and half its time in second structure.



Thus Kekule explained the fact that there is no difference between 1, 2 and 1, 6 positions. Though Kekule's structure can account for the above mentioned properties of benzene but still there are some important characteristics of benzene which could not be explained by these structures. The following characteristics of benzene distinguish it from aliphatic alkenes. These characteristics cannot be explained on the basis of above mentioned structures.

(*i*) Though, benzene has three double bonds, it does not decolourise potassium permanganate and thus is quite stable towards oxidising agents. It does not react immediately with bromine in dilute solution.

(*ii*) Being highly unsaturated benzene tends to undergo electrophilic substitution rather than additon.

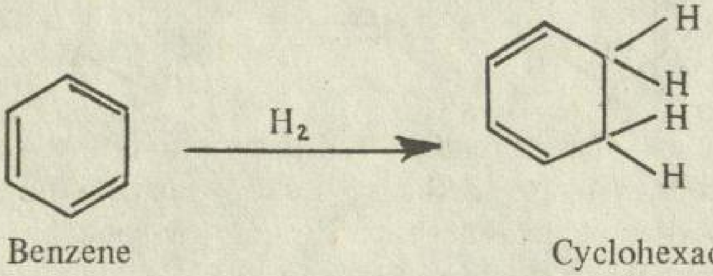
(*iii*) All carbon-carbon bonds in benzene have same bond lengths (1.39 A°) which is less than carbon - carbon single bond (1.54A°)

and greater than carbon-carbon double bond (1.34 A°).

(*iv*) Heats of hydrogenation and heat of combustion of benzene are lower than the calculated values on the basis of Kekule's structures.

(*v*) Hydroxy derivative (phenol) and amino derivative (aniline) of benzene differ in some of their properties from those of alcohols and aliphatic amines.

All the aromatic compounds show more or less all the above mentioned properties. These properties are referred as an aromatic character which distinguishes aromatic compounds from unsaturated aliphatic and alicyclic compounds. Therefore, it may be concluded that π bonds in aromatic compounds are some what different from those of alkenes. It has been observed that when one of the three double bonds of benzene is reduced to single bond the resulting cyclo hexadiene does not show aromatic character and behaves like an ordinary aliphatic diene.



This shows that aromatic character of benzene is due to the special arrangement of electrons in benzene ring.

Modern Concept of the Structure of Benzene.

There are two modern approaches about the structure of benzene.

1. *Orbital Approach* . Each carbon of benzene is linked with three more atoms and so each carbon is [Sp^2] hybridised to give three equivalent coplanar hybridised orbitals. Two of the three hybridised orbitals of each carbon are used to make two sigma bonds with two adjacent carbons. The third hybridised orbital of each carbon makes a sigma bond with a hydrogen. The bond angle between any two sigma bonds is 120°.

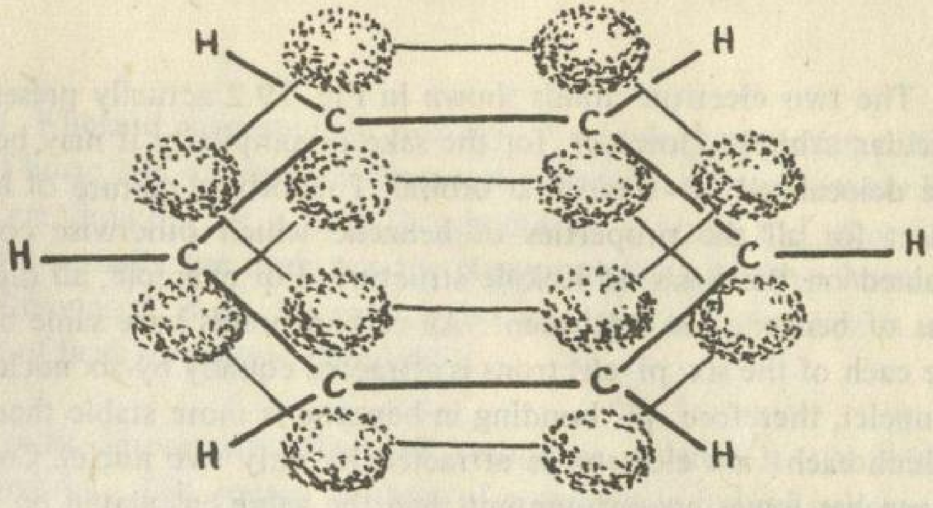
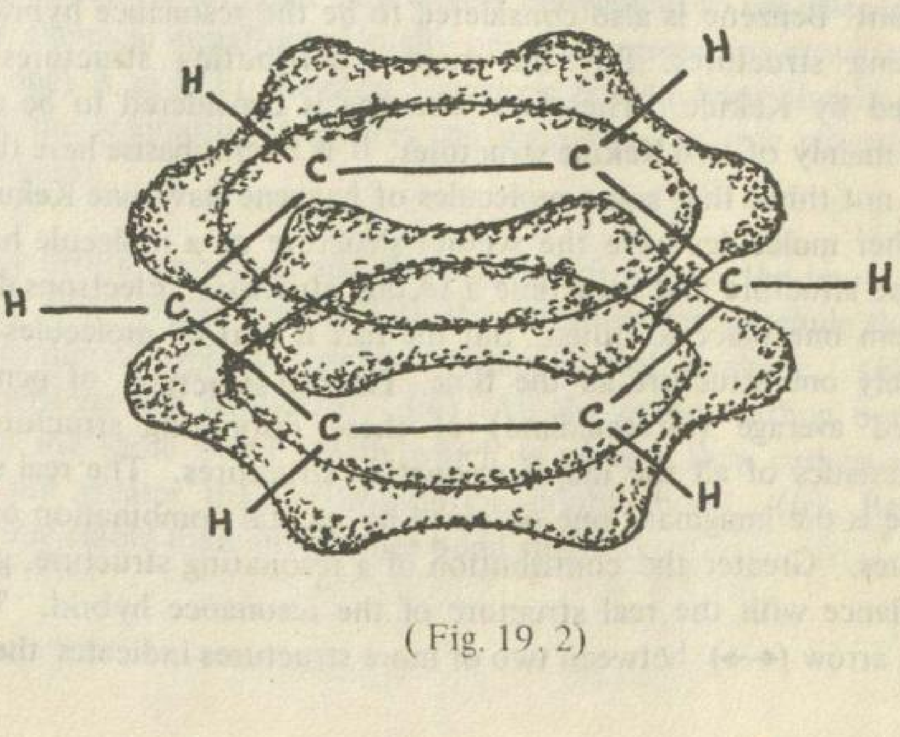


Fig. 19.1

Thus all the six carbons and six hydrogens of benzene are all in one plane and the regular hexagonal ring of bezene is coplanar. Now each carbon of benzene is left with one unhybridised p orbital of which one lobe is above the plane of benzene ring, while the other lobe is below the plane of the ring. Each of these p orbitals contain one electron.

Each p orbital on each carbon overlaps sidewise equally with the p orbitals on each neighbouring carbon forming delocalized π bond which encompasses all the six carbons of benzene. Thus in benzene each pi electron unlike in alkenes; is not localized between two nuclei but all the six pi electrons can be found anywhere in the delocalized orbital. Each electron is equally attracted by each carbon. These electrons make a uniform sheath of electrons above and below the plane of the ring (Figure 19.2).



(Fig. 19. 2)

The two electron clouds shown in Fig. 19.2 actually present three π - molecular orbitals. However, for the sake of simplicity it may be taken as a single delocalized π - molecular orbital. This orbital picture of benzene can account for all the properties of benzene which otherwise could not be explained on the basis of Kekule structure. For example, all the six-carbon atoms of benzene are equivalent. All carbon bonds have same bond length. Since each of the six pi electrons is attracted equally by six nuclei instead of two nuclei, therefore pi bonding in benzene is more stable than in alkenes in which each π - electron is attracted by only two nuclei. Consequently, benzene has lower energy content than the value calculated on the basis of any valence bond structure. Since this difference in energy content is due to delocalization of electrons, therefore, this difference in energy is known as delocalization energy which amounts to 36 K Cals/ mole.

2. *Resonance Theory.* In the previous chapter it has been mentioned that whenever, a molecule can be represented by two or more valence bond structures, it is said to be the resonance hybrid of the contributing structures. These possible structures are called resonating structures. The resonating structures which contribute to the real structure of resonance hybrid differ only in the electronic arrangement but have almost the same relative positions of atoms in space. All the resonating structures may not necessarily contribute equally. Their relative contribution depends upon their relative stability . Greater the stability of a resonating structure, the greater is its contribution. When two or more resonating structures are of equal energy they contribute equally and in such a case resonance is very important. Benzene is also considered to be the resonance hybrid of several resonating structures. But the major contributing structures are those proposed by Kekule. Therefore, benzene is considered to be a resonance hybrid mainly of two Kekule structures. It is to emphasise here that students should not think that some molecules of benzene have one Kekule structure and other molecules have the second structure or a molecule has for some time one structure and sometime a second structure. Electrons do not move also from one place to other. But the fact is that all molecules of benzene have only one structure all the time. The real structure of benzene is the weighted average (intermediate) of these resonating structures and has characteristics of all the major resonating structures. The real structure of benzene is the imaginary one obtained by mental combination of resonating structures. Greater the contribution of a resonating structure, greater is its resemblance with the real structure of the resonance hybrid. The double headed arrow (⟷) between two or more structures indicates the resonance.

G. W. Wheland suggested the analogy of a mule for resonance. Mule is a hybrid of horse and donkey. It does not mean that some mules are horses and some are donkeys or a mule is sometimes a horse and sometimes a donkey. But actually the mule has the characteristics of both a horse and a donkey. Resonance is an important and a common phenomenon which explains lot of facts of organic chemistry.

The most important effect of resonance is that it stabilises the resonance hybrid. The energy content of a resonance hybrid is lower than the calculated value for any resonating structure. The difference in energy content of a resonance hybrid and that of its most stable resonating structure is called *resonance energy* (or delocalization energy in orbital approach).

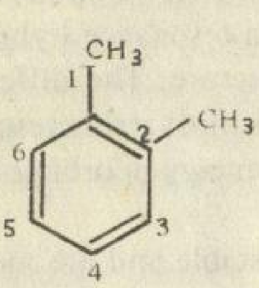
If the resonating structures are more stable and are more nearly equal in stability, the greater will be the resonance energy. Major resonating structures (Kekule's structures) of benzene are equal in stability and are of equal energy. The resonance energy of benzene is 36 K. Cals/mole.

Orbital representation of a molecule is the best description of a compound . The compound can be represented by only one structure in orbital representation but this is not possible in resonance method. It is extremely difficult to visualize the real structure of a resonance hybrid in resonance method. But it is very difficult and time consuming to draw an orbital picture of a molecule in a chemical equation. In resonance method valence bond structures are used so it is very convenient to use valence bond structures in chemical equations. Usually only one resonating structure (the most stable one) is used in chemical equations but students should realize that none of the resonating structures can represent the true structures of a resonance hybrid.

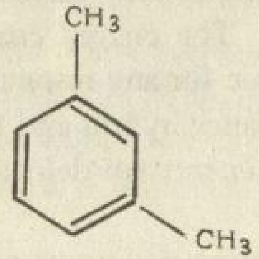
Actually orbital approach and Resonance method are the two ways of explaining the same phenomenon. Both these approaches conclude that (*i*) Benzene molecule is coplanar regular cyclohexagonal in shape. (*ii*) All carbons of benzene are equivalent. (*iii*) All the carbon-carbon bonds in benzene have the same bond length which is smaller than carbon-carbon single bond and greater than carbon-carbon double bond. (*iv*) Benzene molecule is more stable than any valence bond stucture.

Isomerism and Nomenclature.

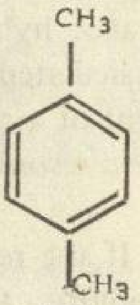
Since all the six carbons in benzene are equivalent, so there is only one mono-substituted product and thus monosubstituted benzenes do not show isomerism. For a disubstituted benzene three isomers are possible depending upon the positions of the substituents. For example there are three isomers of dimethyl benzene.



o - xylene



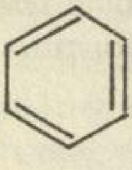
m - xylene



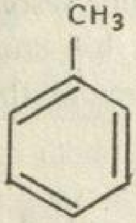
p - xylene

The isomer with substituents at C_1 and C_2 (adjacent carbons) is called *ortho* isomer ; isomer with substituent at C_1 and C_3 (alternate carbons) is called *meta* isomer and the isomer at C_1 and C_4 (opposite) is called *para* isomer. Ortho, meta and para isomers are generally abbreviated by *o*, *m*, and *p* - respectively.

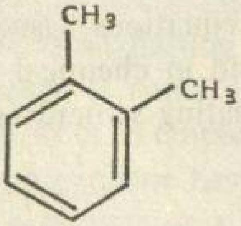
Many of the aromatic hydrocarbons and some derivatives of benzene have common names which are often used as IUPAC system. Some examples of such common names are given below :



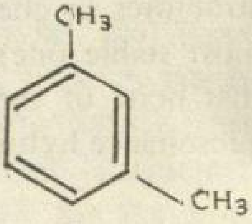
Benzene



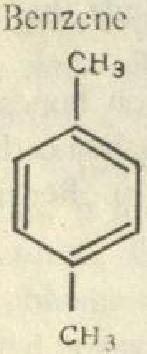
Toluene



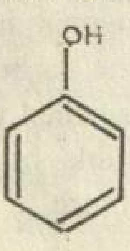
o - xylene



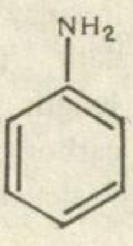
m - xylene



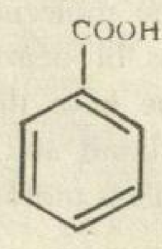
p - xylene



Phenol



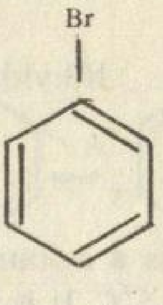
Aniline



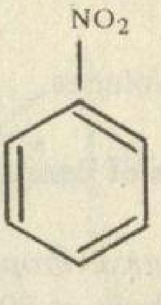
Benzoic acid

For naming mono substituted benzene the name of the substituent is placed before the word benzene.

Examples :



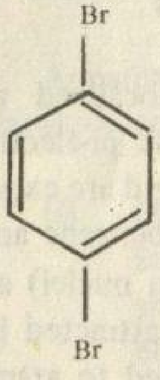
Bromobenzene



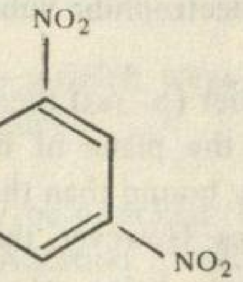
Nitrobenzene

In disubstituted benzenes the positions of substituents are usually indicated by prefixes-ortho, meta and -para.

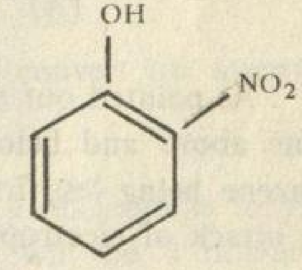
Examples :



p - dibromobenzene



m - dinitro benzene

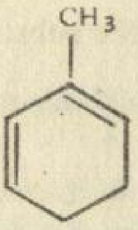


o - nitrophenol

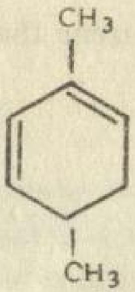
The group C_6H_5 formed by removing one hydrogen from benzene is called the phenyl group which is frequently represented by Ph or Ø.

Homologues of Benzene :

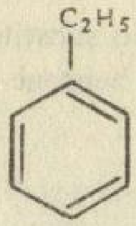
Homologues of benzene are obtained by substituting one or more hydrogens with alkyl groups. Some examples are given below :



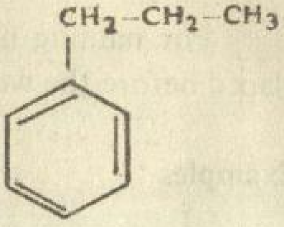
Toluene



p - xylene



Ethyl benzene



Propyl benzene

Properties of Benzene :

Physical Properties : Benzene is a colourless liquid with a peculiar smell. It boils at 80°C and melts at 5.5°C. It is lighter than water (density 0.879) and immiscible with it. Benzene is highly inflammable . Benzene is a very good organic solvent.

Chemical Properties . The most characteristic and important reactions of benzene are electrophilic substitutions. In these reactions aromaticity is retained while in other reactions like oxidation, reduction and addition the aromaticity of benzene is lost.

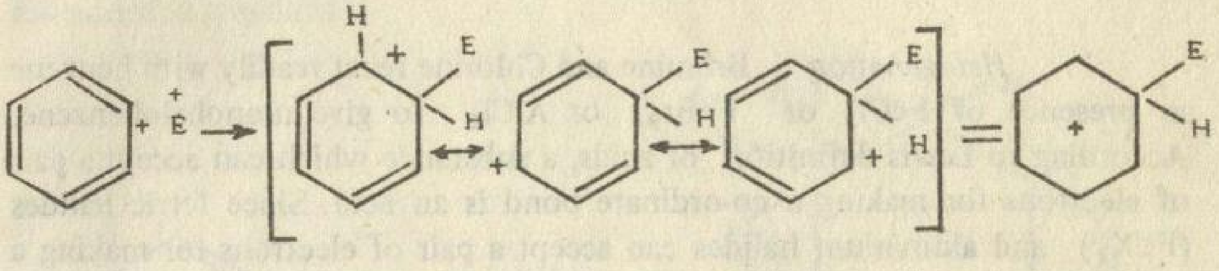
(A) Electrophilic Substitution Reactions

As pointed out earlier (p. 343) there is a cloud of delocalized π - electrons above and below the plane of benzene ring. These pi-electrons of benzene being less firmly bound than the sigma electrons and are exposed to the attack of electrophiles. However, the π electrons of benzene are more firmly bound (each electron being attracted by six carbon nuclei) as compared to the pi-electron of alkenes each electron being attracted by two carbon nuclei). Therefore, stronger electrophiles are needed to attract the benzene ring as compared to alkenes.

Mechanism of electrophilic substiution in benezene involves the following steps.

Ist Step :

In the first step the electrophile attacks the benzene ring producing a carbonium ion (phenonium ion).



(E = an electrophile)

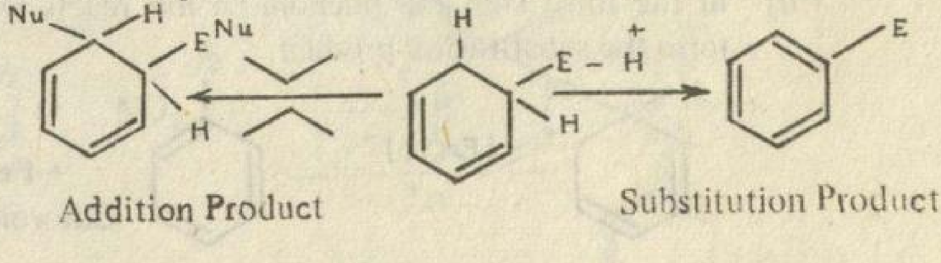
The positive charge of carbonium ion is delocalized over five carbons of benzene ring and this carbonium ion is a resonance hybrid of three main resonating structures as shown above. This delocalization of positive charge renders some stability to the carbonium ion. The intermediate carbonium ion is a non-aromatic species and is unstable as compared to aromatic species.

2nd Step :

Apparently there are two possible ways to convert the intermediate carbonium ion into the final product.

(*i*) Phenonium ion may be attacked by a nucleophile to give 1,2 addition product. Addition product will be a non-aromatic species and will be less stable than aromatic compounds. (See the equation below).

(*ii*) Phenonium ion may lose a proton to give the substitution product. The substitution product will be a typical aromatic compound. For the phenonium ion it is energetically more profitable to lose a proton to give an aromatic substitution product than to give a non-aromatic addition product.

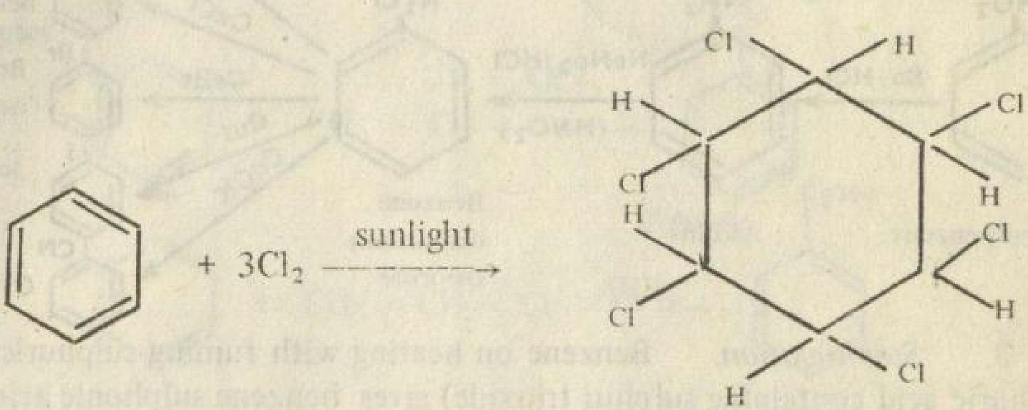


Addition Product

Substitution Product

In these reactions usually metallic iron and chlorine are used instead of ferric chloride and chlorine, chlorine first reacts with iron to form $FeCl_3$.

Chlorination is carried out in the absence of sun light because in the presence of light chlorine adds on benzene to give benzene hexachloride (an addition product).

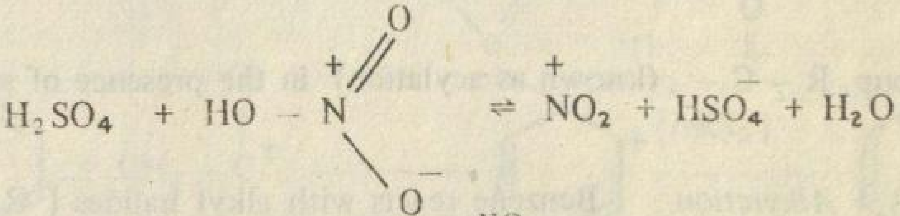


Benzene hexachloride
or
Hexachloro cyclohexane

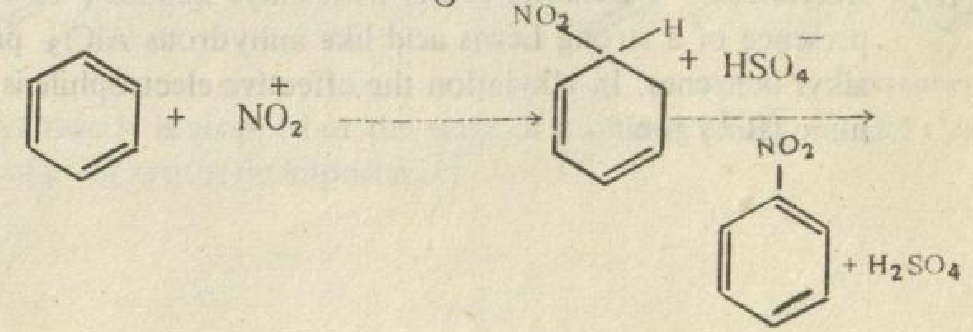
Reaction of fluorine and benzene is too vigorous while with iodine the yield is poor.

2. *Nitration.* Benzene reacts with conc. nitric acid in presence of conc. sulphuric acid to give nitrobenzene. The reaction takes place at about 50°C . Substitution of a nitro group ($-NO_2$) is called nitration.

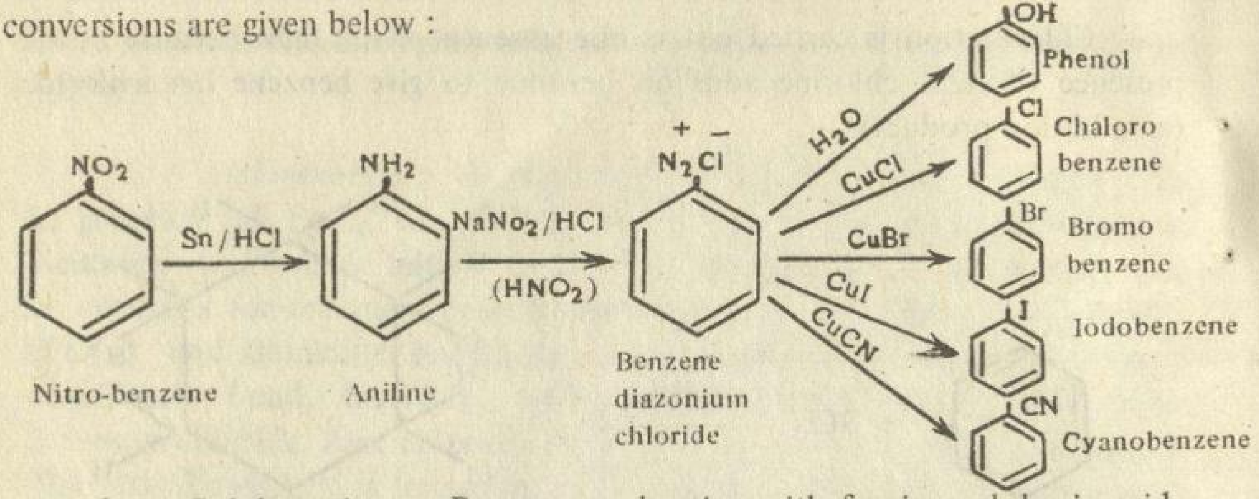
Sulphuric acid reacts with nitric acid to give nitronium ion ($\overset{+}{NO_2}$) : Nitronium ion being a strong electrophile attacks on benzene to give nitrobenzene.

(*i*)


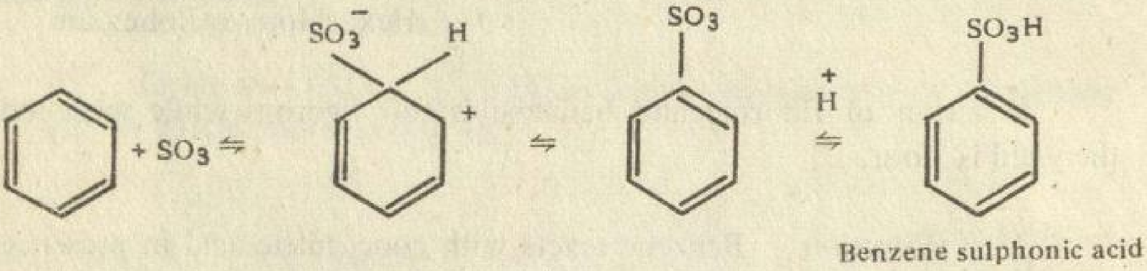
$$H_2SO_4 + HO-\overset{+}{N}(=O)-O^- \rightleftharpoons \overset{+}{NO_2} + H\bar{S}O_4 + H_2O$$

(*ii*)


Nitration is an important reaction because nitrobenzene is also a starting compound for synthesising many substituted products. Some examples of conversions are given below :


NO2
Sn / HCl
NH2
NaNo2/HCl
(HNO2)
+ −
N2Cl
H2O
CuCl
CuBr
CuI
CuCN
OH
Phenol
Cl
Chaloro benzene
Br
Bromo benzene
I
Iodobenzene
CN
Cyanobenzene
Nitro-benzene
Aniline
Benzene diazonium chloride

3. *Sulphonation.* Benzene on heating with fuming sulphuric acid (sulphuric acid containing sulphur trioxide) gives benzene sulphonic acid and the process is known as sulphonation. Sulphur trioxide is believed to be the electrophile which attacks benzene ring.

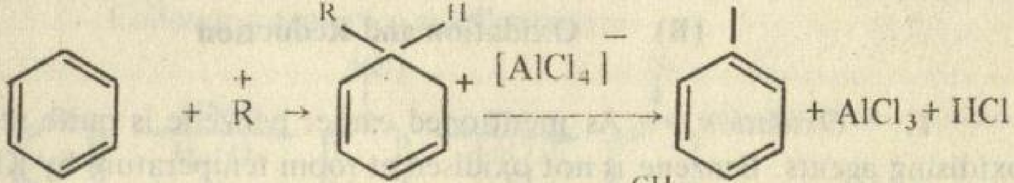

+ SO3 ⇋
SO3−
H
+
⇋
SO3−
+
H
⇋
SO3H
Benzene sulphonic acid

Sulphonic acids are strong acids and their strength lies between sulphuric acid and hydrochloric acid.

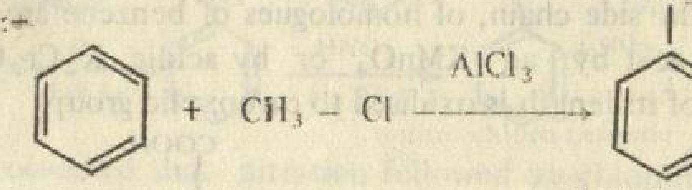
4. *Friedel - Crafts Reaction* : This important reaction involves the substitution of an alkyl group, known as alkylation and substitution of an acyl group, $R-\overset{O}{\overset{\|}{C}}-$, (known as acylation) in the presence of some Lewis acid.

(*i*) *Alkylation.* Benzene reacts with alkyl halides (R − X) in presence of a strong Lewis acid like anhydrous $AlCl_3$ producing alkyl benzenes. In alkylation the effective electrophile is a carbonium (R^+) ion.

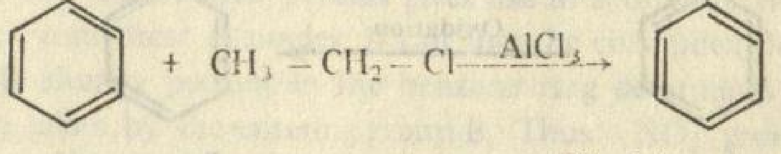
$$R-Cl + AlCl_3 \rightleftharpoons \overset{+}{R} + [AlCl_4]^{-}$$


R
H
+
R
+
[AlCl4]
−
R
+ AlCl3 + HCl

Examples :-


CH3
AlCl3
+ CH3 − Cl

Toluene

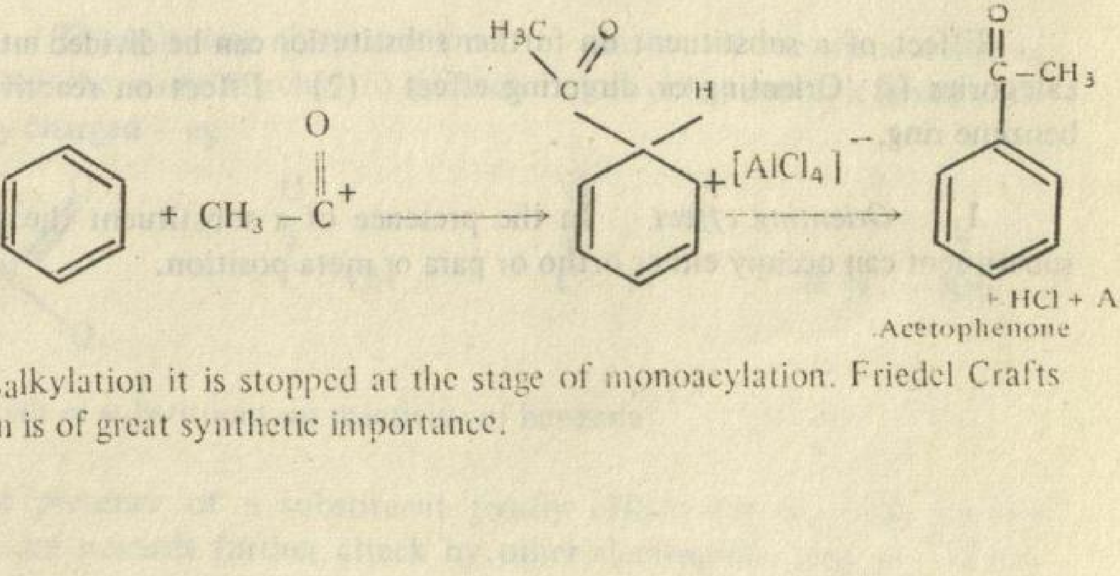

C2H5
+ CH3 − CH2 − Cl
AlCl3

Ethyl benzene

The main difficulty with alkylation is that reaction does not stop at the stage of monoalkylation but polyalkylation products are obtained.

(*ii*) *Acylation.* Benzene reacts with acyl halides ($R-\overset{O}{\overset{\|}{C}}-Cl$) in presence of Lewis acid forming ketones. In this reaction of acylation the effective electophile is acylium ion ($R-\overset{O}{\overset{\|}{C}}+$)

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + AlCl_3 \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}^{+} + [AlCl_4]^{-}$$


O
+ CH3 − C+
H3C
O
C
H
+
[AlCl4]
−
O
C − CH3

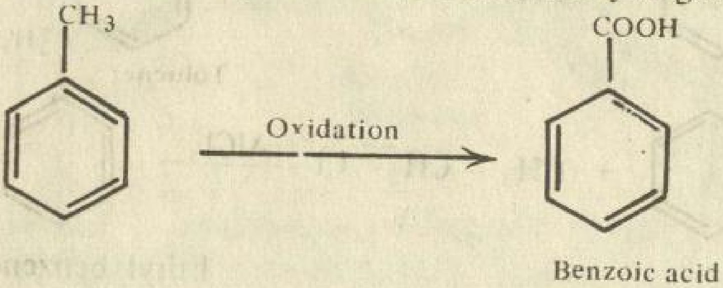
+ HCl + AlCl3

Acetophenone

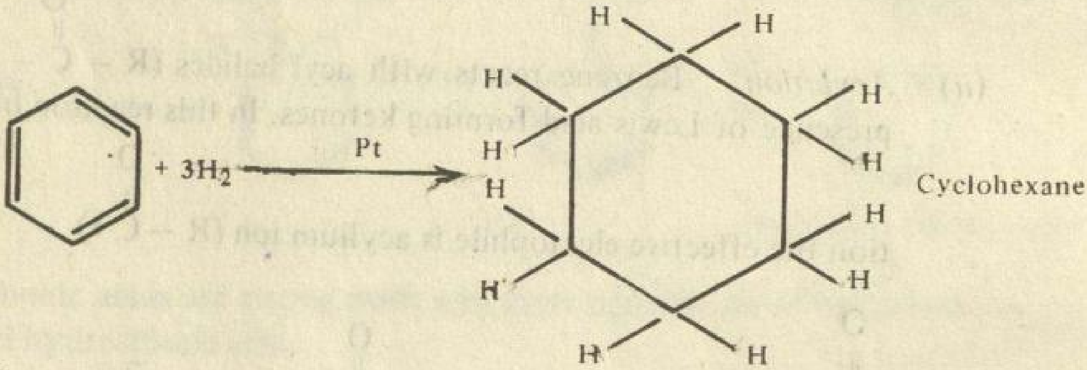
Unlike-alkylation it is stopped at the stage of monoacylation. Friedel Crafts reaction is of great synthetic importance.

(B) Oxidation and Reduction

1. *Oxidation.* As mentioned earlier benzene is quite resistant to oxidising agents. Benzene is not oxidised at room temperature by $KMnO_4$ or $K_2Cr_2O_7$. However, the side chain, of homologues of benzene are oxidised easily into carboxylic acid by aq $KMnO_4$ or by acidic $K_2Cr_2O_7$. The side chain irrespective of its length is oxidised to carboxylic group.



2. *Reduction.* Benzene is reduced by catalytic hydrogenation into saturated cyclohexane.

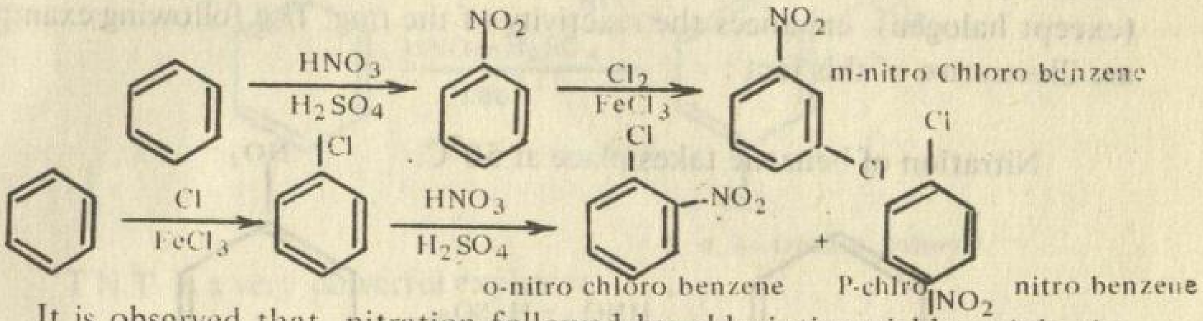


Effect of a substituent on further substitution :

Effect of a substituent on further substitution can be divided into two categories (i) Orienting or directing effect (2) Effect on reactivity of benzene ring.

1. *Orienting effect.* In the presence of a substituent the second substituent can occupy either ortho or para or meta position.

Following examples are illustrative.



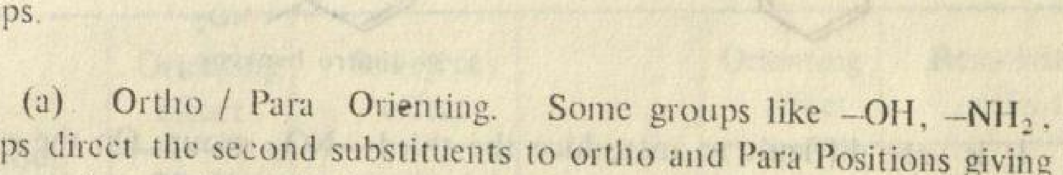
It is observed that nitration followed by chlorintion yields mainly the meta-isomer, but the reverse process gives rise to a mixture of ortho- and para-isomers. From these examples, it can then be concluded that the Group A which is already present in the benzene ring determines the position which will be taken by the entering group B. Thus $-NO_2$ group directs the $-Cl$ group to meta-position, whereas the Cl-group directs the $-NO_2$ group to ortho – and Para-positions.

According to orienting effect the substituents can be divided into two groups.

(a) Ortho / Para Orienting. Some groups like $-OH$, $-NH_2$, $-R$ groups direct the second substituents to ortho and Para Positions giving the mixture of o– and p disubstituted derivatives and these groups are called o– and p–Orienting.

(b) Meta Orienting. Some groups like $-NO_2$, $-COOH$ and $-CHO$ groups direct the second substituent to meta - positions. These are called meta Orienting groups.

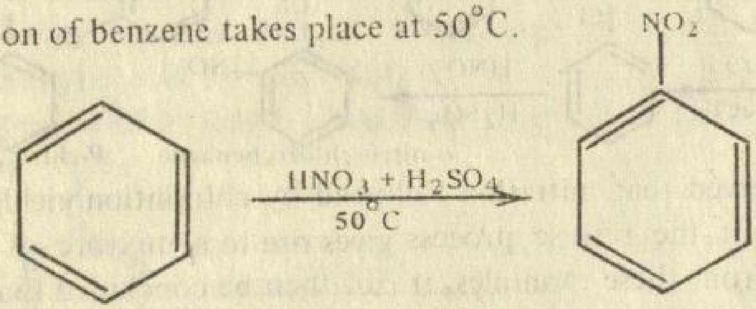
There is one thing common in almost all the meta-orienting groups that the atom attached to benzene ring is either multiple bond or is positively charged – eg.


$-\overset{\overset{O}{\|}}{C}-OH \qquad -\overset{\overset{O}{\|}}{C}-H \qquad -C\equiv N;\ -\overset{+}{N}H_3$

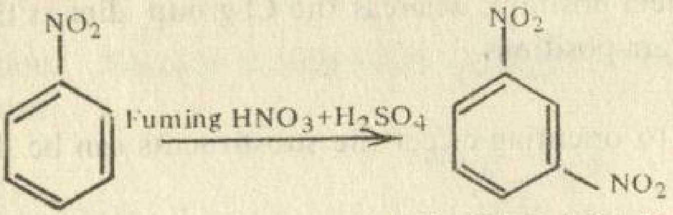
2. Effect of substituent on reactivity of benzene.

The presence of a substituent greatly effects the reactivity of the banzene ring towards further attack by other electrophilic reagents. It has been observed that a meta-directing group, if present, greatly reduces the reactivity of benzene ring. Whereas, an ortho – or para-directing group (except halogen) enhances the reactivity of the ring. The following examples are illustrative of this fact :

Nitration of benzene takes place at 50°C.

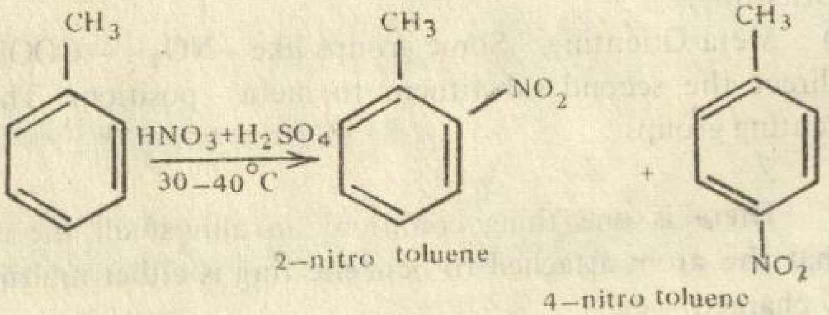

NO_2
$HNO_3 + H_2SO_4$
$50^\circ C$

For dinitration fuming HNO_3 at higher temperature has to be employed :


NO_2
Fuming HNO_3+H_2SO_4
NO_2
NO_2

1, 3–dinitro benzene

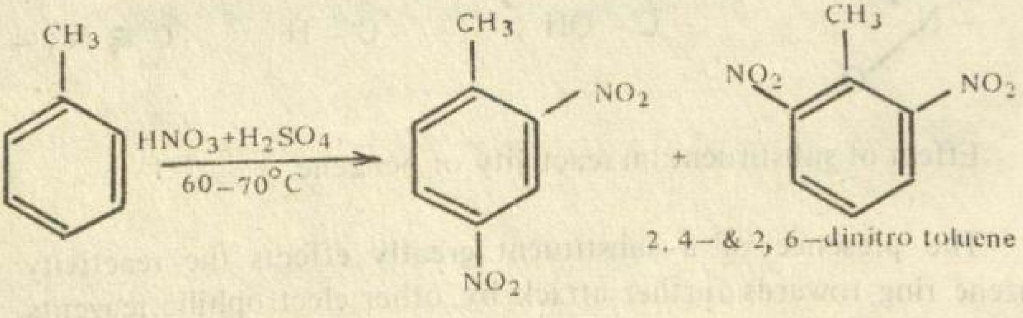
It is very difficult to introduce the third $-NO_2$ group. On the other hand nitration of toluene takes place with HNO_3 and H_2SO_4 mixture at 30 – 40°C.


CH_3
HNO_3+H_2SO_4
30–40°C
CH_3
NO_2
+
CH_3
NO_2

2–nitro toluene

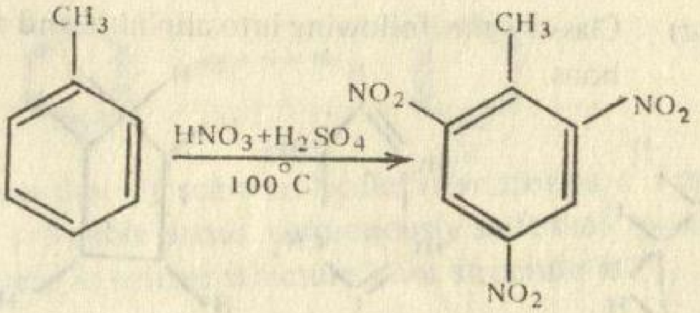
4–nitro toluene

If the temperature is raised to 60 – 70°C, di-nitro rather than mono nitro– toluenes are obtained.


CH_3
HNO_3+H_2SO_4
60–70°C
CH_3
NO_2
NO_2
+
CH_3
NO_2
NO_2

2, 4– & 2, 6–dinitro toluene

and if the reaction is performed at 100°C, the activating influence of the methyl group is so strong that, 2, 4, 6-trinitro toluene is formed.



2, 4, 6–trinitro tolnene.

T N T is a very powerful explosive.

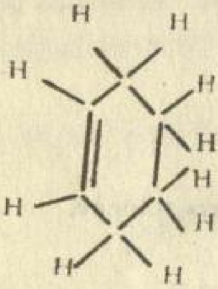
Therefore, it may be remembered that an ortho or a para directing group (except halogen), if present activates the benzene ring and makes an electrophilic attack much easier, whereas a meta directing group deactivates the benzene ring and makes further electrophilic attack difficult.

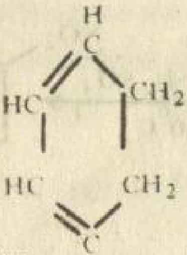
Orienting and reactivity effects of some important groups are given in the following table :-

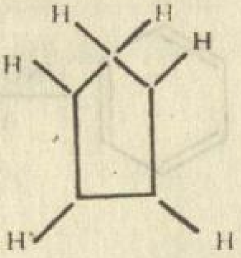
Group	Orienting effect	Reactivity effect	Group	Orienting effect	Reactivity effect
	o/p Orienting	Activating group		m-orienting	De-activating group
$-OH$	o/p	"	$-CH_2Cl$	"	"
$-NH_2$	o/p	"	$-NO_2$	"	"
$-R$(alkyl group)	"	"	$-COOH$	"	"
$-OR$	"	"	$-CHO$	"	"
$-C_6H_5$	"	"	$-C\equiv N$	"	"
$-NR_2$	"	"	$-SO_3H$	"	"
Halogen	"	Deactivating group	$-\overset{\overset{O}{\parallel}}{C}-R$	"	"
			$-CF_3$	"	"
			$-CCl_3$	"	"
			$-\overset{+}{N}H_3$	"	"

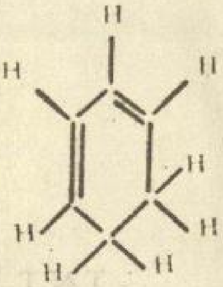
QUESTIONS

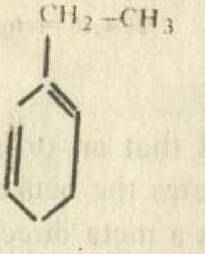
1. (*a*) Classify the following into aliphatic and aromatic hydrocarbons.

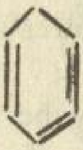












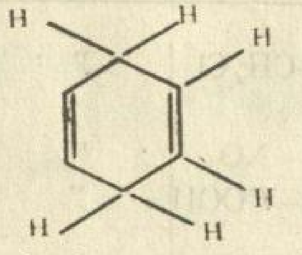
(*b*) Have all the aromatic compounds fragrant odour ? What is the main source of aromatic compounds ? What are the main fractions obtained from fractional distillation of coal-tar ?

2. What are the facts against the following proposed structures of benzene ?

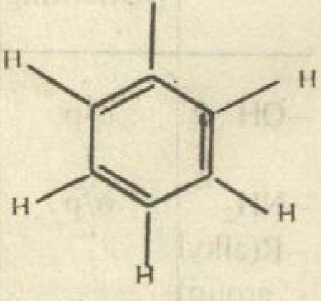
(*i*) $CH_2 = CH - CH = C = C = CH_2$

(*ii*) $CH_2 = CH - C \equiv C - CH = CH_2$

(*iii*)



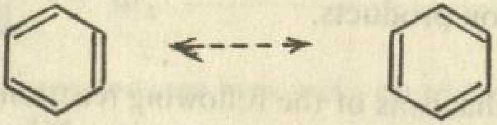
(iv)



3. What is the aromatic character that distinguishes the aromatic compounds from aliphatic compounds ? Can any of the Kekule's structures explain the aromatic character. ?

4. Do all the carbons and hydrogens of benzene lie in one plane ? Suppose carbons are in different planes, will it be possible for benzene to show resonance or will it be possible, for carbons of the benzene to overlap mutually their unhybridised p-orbitals ? Explain your answer.

5. According to resonance approach benzene is resonance hybrid of the following two main structures.



I II

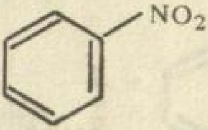
Does it mean that (*i*) some molecules have structure I and some have structure II. (*ii*) Double bonds continuously shift their position, (*iii*) real structure of benzene is neither structure I nor structure II ?

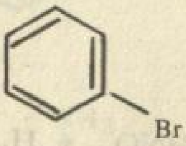
6. How does orbital approach explain the aromatic character of benzenes ? Do all the six electrons of benzene occupy a single molecular orbital ?

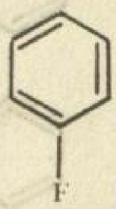
7. What do you understand by delocalization of electrons in benzene? How does this delocalization explain the lower energy and stability of benzene?

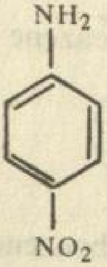
8. Explain whether the π - electrons of benzene are more susceptible to an electrophilic attack or π - electrons of ethene. Draw the diagram of delocalized π - electrons of benzene.

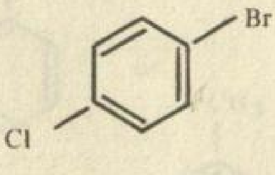
9. (a) Give the names of the following compounds :

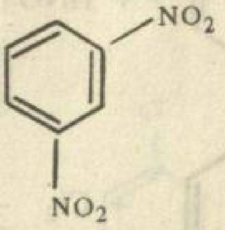


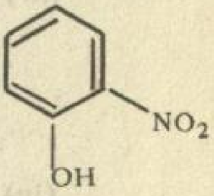












(*b*) Write the structures of the following compounds.

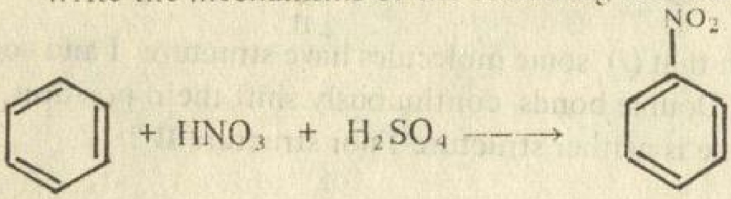
m - bromobenzoic acid ; o - difluorobenzene ; p - nitrotoluene ; o - bromophenol.

10. Write chemical equations for the conversion of benzene into nitrobenzene, benzene sulphonic acid, toluene, bromobenzene and acetophenone.

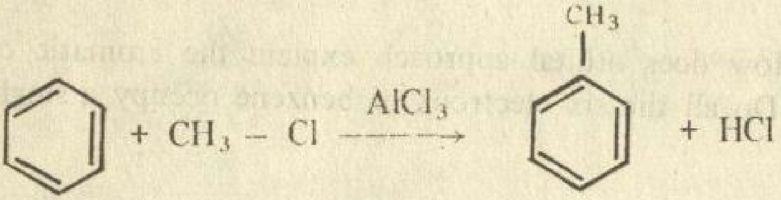
11. (a) Explain the fact that benzene gives normally substitution products instead of addition products.

(*b*) Write the mechanisms of the following reactions :

(*i*)

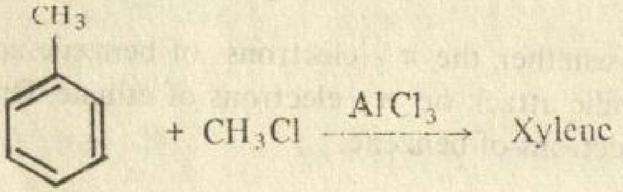

+ HNO_3 + H_2SO_4
NO_2

(*ii*)

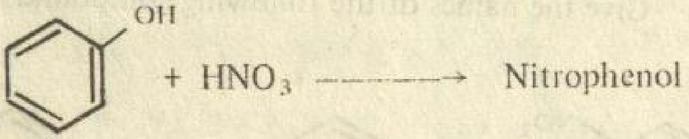

+ $CH_3 - Cl$
$AlCl_3$
CH_3
+ HCl

12. Write the structure of the products in the following reaction :

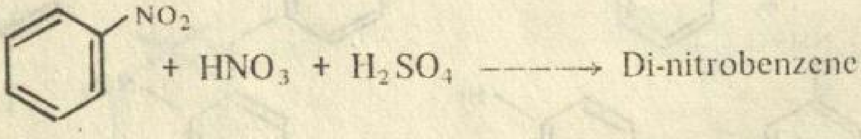
(*i*)


CH_3
+ CH_3Cl
$AlCl_3$
Xylene

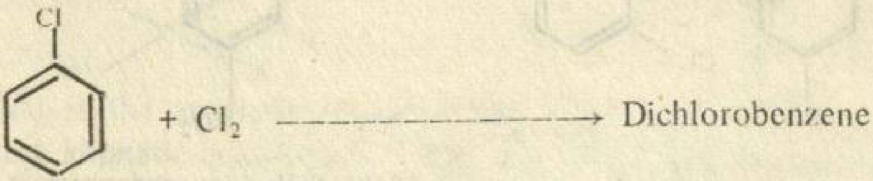
(*ii*)


OH
+ HNO_3
Nitrophenol

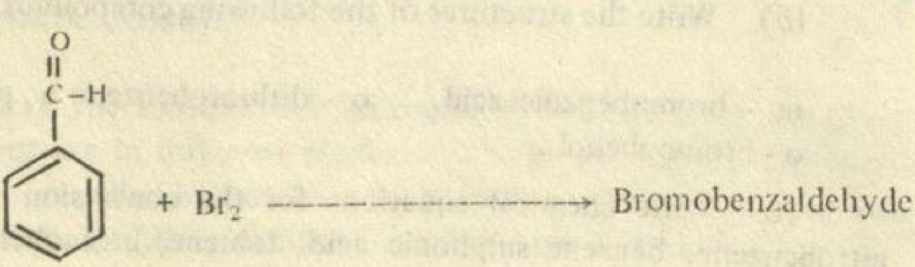
(*iii*)

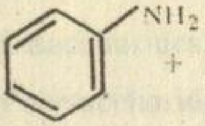

NO_2
+ HNO_3 + H_2SO_4
Di-nitrobenzene

(*iv*)

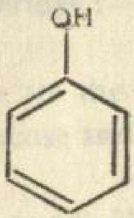

Cl
+ Cl_2
Dichlorobenzene

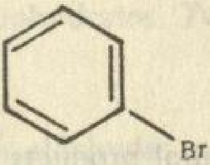
(*v*)

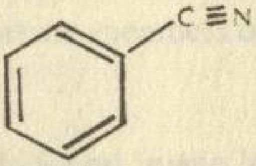

O
C–H
+ Br_2
Bromobenzaldehyde

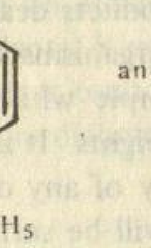
(*vi*)  + Br_2 ——————→ Bromoaniline

13. Starting from benzene how will you obtain the following :

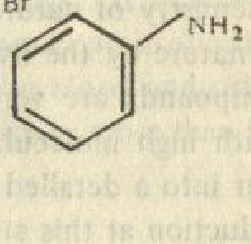




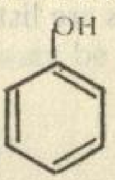
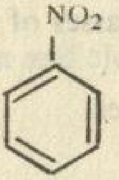


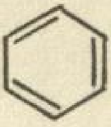
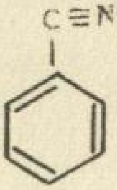


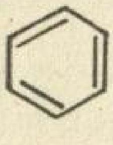
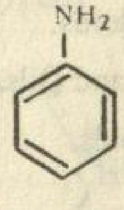
and

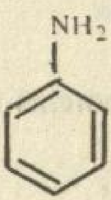
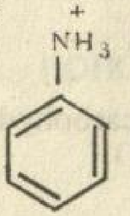


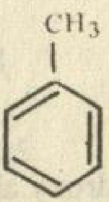
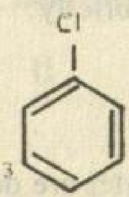
14. In each of the following pairs in which compound further electrophilic substitution will be easier ?

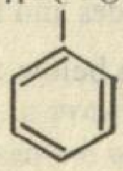
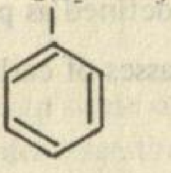
(i)  or 

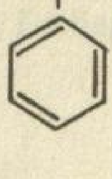
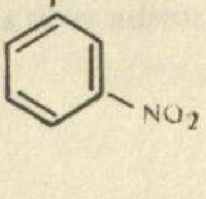
(ii)  or 

(iii)  or 

(iv)  or 

(v)  or 

(vi)  or 

(vii)  or 

CHAPTER 20

NATURAL PRODUCTS

The chemistry of natural products deals with the chemical compounds produced in nature by the living organisms such as plants and animals. Some of these compounds are very simple while others are highly complicated molecules with high molecular weights. It is beyond the scope of this text-book to enter into a detailed study of any one of these compounds. A very simple introduction at this stage will be sufficient to introduce the students with this important branch of chemistry.

Some important classes of the natural products are listed below :

1. Carbohydrates.
2. Vitamins.
3. Proteins.
4. Alkaloids.
5. Fats and Oils.
6. Steroids.

In this chapter only carbohydrates, vitamins, proteins and alkaloids will be discussed briefly.

Carbohydrates

Carbohydrates are defined as polyhydroxy aldehydes and ketones.

Three important classes of carbohydrates are given below :–

(*i*) Monosaccharides

(*ii*) Disaccharides

(*iii*) Polysaccharides.

Monosaccharides :–

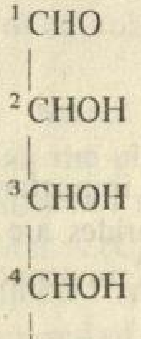
These are the simplest carbohydrates. Two important members of this class are glucose and fructose.

Glucose ($C_6H_{12}O_6$) is an aldehydic sugar. It is found in the leaves, flowers and fruits of many plants. Ripe grapes contain about 20 – 30% of glucose. In small quantity it is found in the blood and urine of man. The urine of a patient suffering from diabetes contains more than 80% of glucose.

Glucose serves as a quick source of energy, because it is absorbed directly through the intestinal walls without prior digestion.

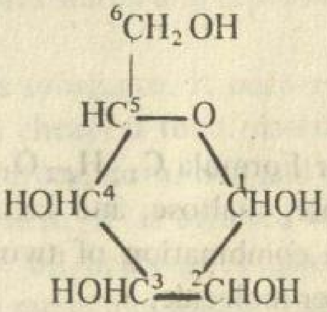
Glucose may be represented by open and closed chain structures:

(Structure I, II) :



$$\begin{array}{l} ^{1}CHO \\ | \\ ^{2}CHOH \\ | \\ ^{3}CHOH \\ | \\ ^{4}CHOH \\ | \\ ^{5}CHOH \\ | \\ ^{6}CH_2OH \end{array}$$

I

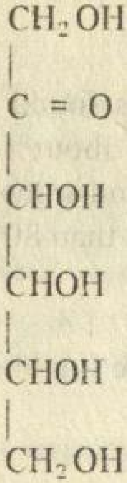


II

Due to presence of aldehydic group some of the chemical properties of glucose resemble with those of aldehydes (see the properties of aldehydes) For example it reduces Fehling's solution and gives silver mirror test.

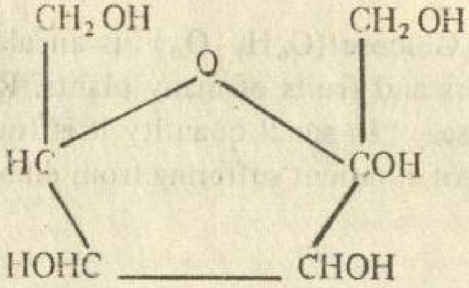
Fructose ($C_6H_{12}O_6$) :–

It is the sweetest of all sugars and occurs in all fruits and honey. Fructose has a ketonic group, thus resembling in some of its properties with those of **ketones** (see properties of Ketones). Like glucose it can also be represented by open chain (III) and close chain (IV) structures.



$$\begin{array}{c} CH_2OH \\ | \\ C=O \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

III



IV

Fructose and glucose have the same molecular formula and are therefore isomers.

Disaccharide :–

Molecular Formula $C_{12}H_{22}O_{11}$. The most important members of this class are sucrose, maltose, and lactose. Disaccharides are considered to be formed by the combination of two molecules of monosaccharides with the loss of one water molecule.

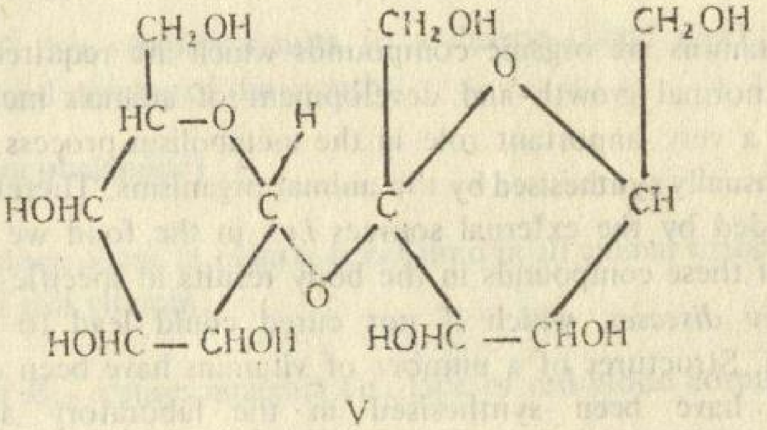
$$2\,C_6H_{12}O_6 \xrightarrow{-H_2O} C_{12}H_{22}O_{11}$$

Therefore, disaccharides on hydrolysis with dil. acids or enzymes yield two molecules of monosaccharides e.g.,

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{enzyme}]{\text{dil. Acid}} \underset{\text{Fructose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

Sucrose is found in sugar-cane and sugar beet whereas lactose is present in the milk of all mammals. Maltose is found in barley.

The structure of sucrose is given below.



Polysaccharides :–

Formula $(C_6H_{10}O_5)n$

This class of carbohydrates includes starch and cellulose.

Starch . Starch is amorphous substance. It occurs in the tubers and seeds of nearly all the plants. It is the cheapest food material for the human beings. Main sources of starch are potatoes, corn, rice and wheat. Molecular formula for starch is $(C_6H_{10}O_5)_n$ where n is believed to be about 3000. Starch on complete hydrolysis with dil. acids gives glucose. Thus starch molecule is composed of many glucose molecules linked together.

Cellulose. Formula $(C_6H_{10}O_5)n$. It is the most widely distributed polysaccharides. It constitutes a large part of wood and other matters of vegetable origin. Cotton is almost pure cellulose. Similarly a good quality paper is almost 100% cellulose.

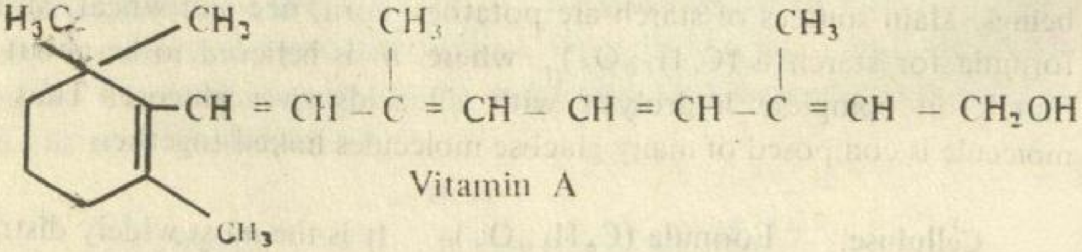
Cellulose molecule is very large with molecular weight running into hundreds of thousands. The fact that cellulose is a carbohydrate is demonstrated by the hydrolysis of saw dust with dil. acids to glucose. The structure of cellulose is similar to that of starch. However, the molecule of cellulose is much larger than that of starch.

VITAMINS

Vitamins are organic compounds which are required in small amount for the normal growth and development of animals including man. They perform a very important role in the metabolism process. These substances are not usually synthesised by the animal organisms. Therefore vitamins must be provided by the external sources *i.e.*, in the food we eat. Lack or deficiency of these compounds in the body results in specific diseases known as *deficiency diseases*, which if not cured could lead to the death of the organism. Structures of a number of vitamins have been determined. Some vitamins have been synthesised in the laboratory and are available commercially to supplement our diet. Since most of the vitamins have complex structure, therefore, for the sake of simplicity they have been named as A, B, C, D etc. A few are discussed here in brief.

Vitamin A, $C_{20}H_{30}O$:

It occurs in fish oils, green vegetables, carrots, tomatoes, egg yolk, milk and butter. Deficiency of Vitamin A causes night blindness. Also the skin and hair get dry and the resistance of the body to infections is lowered.



Vitamin A

Vitamin B_1 (Thiamine), $C_{12}H_{17}N_4SCl$:

Eggs, meat, peas and yeast are the main sources of Vitamin B_1.

Deficiency of Vitamin B_1 results in a disease called *Beriberi*. A person suffering from this disease feels mental and physical fatigue, fear and nervousness.

Vitamin B_2 (Riboflavin), $C_{17}H_{20}O_6N_4$:

It occurs in yeast, liver, milk, fish and green vegetables. It was first isolated from whey (لسّی).

Deficiency of this vitamin results in a disease called *chellosis i.e.*, cracking of the lips and corners of the mouth.

Vitamin B_{12} (Cyanocobalamine) :–

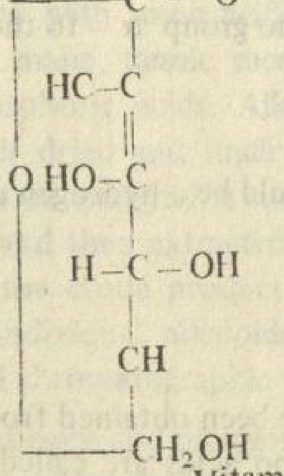
The vitamin does occur in plants. It is found in all animal tissues. Liver is the best source of this vitamin.

Deficiency of B_{12} causes anaemia *i.e.*, lack of red blood corpuscles in the blood.

Vitamin C (Ascorbic Acid), $C_6H_8O_6$:

The best sources of vitamin C are citrus fruits and tomatoes.

Deficiency disease of vitamin C is called *scurvy*. A person suffering from scurvy feels weakness, aching in bones and the skin gets dry and rough. In severe cases the gums swell and bleed very easily and the teeth become loose.



Vitamin C

Vitamin D :

Two important members of this group are given below :–

Vitamin D_2 $C_{28}H_{44}O$:

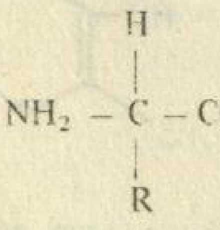
Ergosterol which is present in animal fats is converted to vitamin D_2 by ultraviolet light irradiation. D_2 is present in milk, egg yolk and yeast.

Vitamin D_3 :

The ultra violet light present in the sun rays acts on cholesterol of our body and converts it into D_3 . The best source of D_3 is the liver of cod. Deficiency disease of vitamin D_2 and D_3 is called Rickets. Rickets is the disease of bones, in which the bones are soft and are easily deformed when subjected to stress.

Proteins : Just as cellulose is the building material for plants, similarly proteins are the building material for all living cells. Muscles, skin, hair, nail enzymes, feathers, wool, all are examples of proteins. Molecular Wts. of proteins are very high ranging from 20,000 to 20,000,000. They consist of carbon, hydrogen, oxygen and nitrogen. Some proteins contain sulphur as well. Since they are high molecular wt polymers they do not have definite m.p., and are difficult to crystallise.

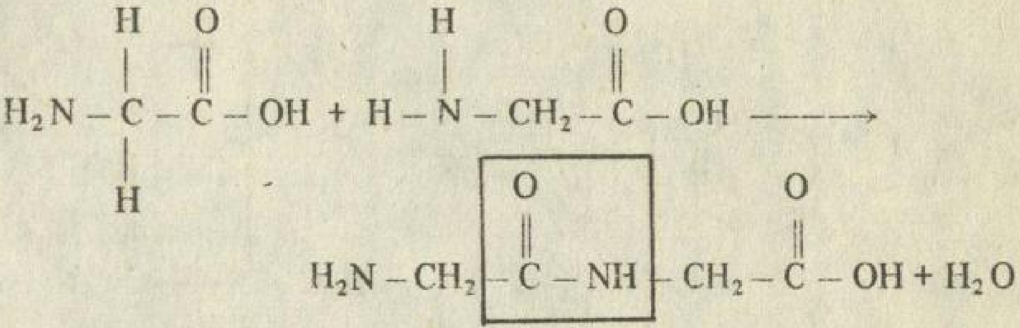
Proteins on hydrolysis with acids or alkalies or certain enzymes give α-amino acids *i.e.*, the acids containing amino group α – to the carboxyl group



e.g., $NH_2 - \overset{H}{\underset{R}{C}} - COOH$, where R could be a hydrogen as in glycine or it could be any other group.

Some 30 different amino acids have been obtained from the hydroylsis of different proteins. Ten of these amino acids are called *essential amino acids* i.e., they cannot be synthesised by the body and absence of any one of them prevents normal growth in the body and causes death.

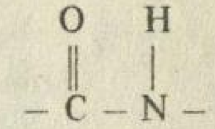
According to a theory of protein structure, many simple amino acids combine together to give large molecules of proteins e.g., two molecules of glycine combine together to give a compound called glycyl glycine.



$$H_2N-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OH + H-\overset{\overset{H}{|}}{N}-CH_2-\overset{\overset{O}{\|}}{C}-OH \longrightarrow$$

$$H_2N-CH_2-\boxed{\overset{\overset{O}{\|}}{C}-NH}-CH_2-\overset{\overset{O}{\|}}{C}-OH + H_2O$$

Glycyl Glycine



Thus different amino acids are linked together through $-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-$ called *peptide linkage*, and the product is called peptide. For example glycyl glycine is a dipeptide. If many of these simple amino acids, combine together through peptide linkages, the product is a polypeptide. These chains of polypeptides are then linked together through various mechanisms into specific layers, giving rise to a definite structure of a protein molecule.

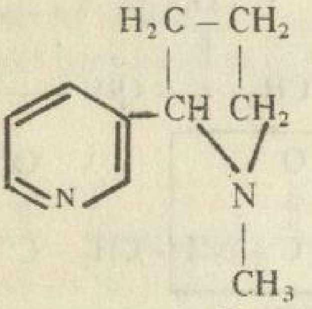
Alkaloids. Alkaloids are the nitrogenous heterocyclic compounds of plant origin. They are mostly found in the roots, leaves and seeds of the flowering plants. As a rule alkaloids are not found in free form in the plants but are combined with some acids in the form of the salts. Such common acids are citric, malic, tannic succinic, oxalic, as well as sulphuric, hydrochloric and phosphoric acids. Alkaloids may be obtained from plants by extracting the air dried and finally powdered material with ethanol. Some times the powdered material is made alkaline to liberate the free alkaloids from their salts and then extracted with ether or ethyl acetate. The solvent is evaporated and the crude product which is usually mixture of alkaloids is separated into individual alkaloids by fractional crystallization, fractional precipitation and chromatographic techniques.

Carbon, hydrogen and nitrogen are generally present in alkaloids. A few alkaloids are known that do not contain oxygen *e.g.*, nicotine. The alkaloids are crystalline solids and liquids. Alkaloids have a marked physiological effect on the organism.

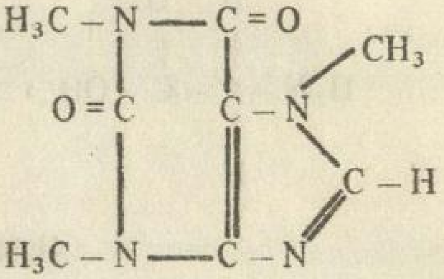
A few alkaloids are given below :–

1. **Nicotine.** $C_{10}H_{14}N_2$:–

It is a colourless oil, b.p. 246°. It is obtained from tobacco,



Nicotine



Caffeine

2. **Caffeine** $C_8H_{10}N_4O_2$:-

It is the principal alkaloid of coffee and tea. Coffee beans may contain 1% of caffeine and tea leaves 2–4%.

3. Morphine $C_{17}H_{19}NO_3$.

It is found in opium upto 10–12%.

QUESTIONS

1. What are the important classes of organic compounds? What are the building materials of plants and animals?

2. What vitamin will you suggest to the persons suffering from the following diseases :

(*i*) Beriberi

(*ii*) Scurvy

(*iii*) Night blindness

(*iv*) Anaemia

Why is it good for health to sit in sun ?

3. What are the functional groups in glucose ? What monosaccharides are obtained on the hydrolysis of sucrose, maltose, starch and cellulose? Name the isomers of fructose and maltose ?

4. Are the alkaloids acidic or basic in nature ? What is the impor-

tance of alkaloids for man ? How are alkaloids extracted ? Name the alkaloids found in tabacco, opium and tea leaves.

5. What are the basic units of proteins ? How are these units linked together in proteins ? Can our body synthesise all the amino acids found in proteins ? Write the structure of simplest acid found in proteins ?

– – –

THE END

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